

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS ON ORGANIC CHEMISTRY.

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ON

PHYSICAL, INORGANIC, MINERALOGICAL, PHYSIOLOGICAL, AGRICULTURAL, AND ANALYTICAL CHEMISTRY.

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Configuration of Fatty Compounds. By PAVEL IW. PETRENKO-KRITSCHENKO (*J. pr. Chem.*, 1900, [ii], 315—320).—A continuation of the controversy between the author (*Abstr.*, 1900, i, 421) and Krafft (*ibid.*, 577).R. H. P.

The Geometrically Isomeric Symmetrical Dimethylethylenes (ψ -Butylenes), their Bromo-derivatives, and β -Bromomonocarboxylic acids. By JOHANNES WISLICENUS (*Annalen*, 1900, 313, 207—209).—An introduction to the following two papers, of which the first comprises revision of a previous paper on the same subject (*Hölz*, *Abstr.*, 1889, 575).M. O. F.

Derivatives of ψ Butylene Dibromide and Crotonylene Hydrobromide. By JOHANNES WISLICENUS and PAUL SCHMIDT (*Annalen*, 1900, 313, 210—228).—The authors have prepared considerable quantities of ψ -butylene by the method of Le Bel and Greene, which consists in allowing *isobutyl* alcohol to drop on fused zinc chloride, and absorbing the *isobutylene* with sulphuric acid; the hydrocarbon thus ob-

tained is a mixture of the centro symmetrical ψ -butylene, $\begin{array}{c} \text{CH}_3 \cdot \text{C} \cdot \text{H} \\ | \\ \text{H} \cdot \text{C} \cdot \text{CH}_3 \end{array}$,

with the plano-symmetrical hydrocarbon, $\begin{array}{c} \text{CH}_3 \cdot \text{C} \cdot \text{H} \\ | \\ \text{CH}_3 \cdot \text{C} \cdot \text{H} \end{array}$, in the proportion 1:2. The dibromide obtained when this mixture combines with bromine is separable into two fractions, of which that having the higher boiling point (158—159°), when decomposed with potassium

hydroxide (1 mol.), yields plano-symmetrical bromo- ψ -butylene(!), $\text{CH}_3 \cdot \overset{\text{CH}_3 \cdot \text{C} \cdot \text{H}}{\underset{\text{CH}_3 \cdot \text{C} \cdot \text{Br}}{\text{C}}}$, in larger amount than the lower fraction (157—158°), but

in both fractions the centro-symmetrical isomeride, $\text{CH}_3 \cdot \overset{\text{CH}_3 \cdot \text{C} \cdot \text{H}}{\underset{\text{Br} \cdot \text{C} \cdot \text{CH}_3}{\text{C}}}$, preponderates; only 15 per cent. of the latter is attacked after 1 hour with 15 per cent. alcoholic potash, whereas the plano-symmetrical derivative is thereby completely resolved into crotonylene. In other words, of the greater part of the ψ -butylene dibromide, one-third is converted into the plano-symmetrical bromo- ψ -butylene, the remaining two-thirds yielding the centro-symmetrical modification.

The boiling point of the centro-symmetrical bromo- ψ -butylene is certainly not lower than 93—94°, but the presence of hydrogen bromide induces transformation into the plano-symmetrical modification; this change takes place at the ordinary temperature, and is accelerated by sunlight, and the boiling point therefore becomes depressed. The plano-symmetrical modification has an agreeable odour when freshly prepared, boils at 83·5—84·5°, and has a sp. gr. 1·3152 at 26°/4°; when exposed to light, it acquires a disagreeable odour, and, hydrogen bromide being eliminated, undergoes transformation into the centro-symmetrical modification, but not to so great an extent as in the converse case.

Ethylacetylene [butinene], C_2H_3 , is a colourless, very limpid liquid which boils at 17—18°; it yields explosive precipitates with ammoniacal silver chloride and alcoholic silver nitrate solutions. Dimethylacetylene or crotonylene, $\text{CMe}:\text{CMe}$, boils at 27·2—27·6°.

Plano-symmetrical crotonylene dibromide, $\text{CH}_3 \cdot \overset{\text{CH}_3 \cdot \text{C} \cdot \text{Br}}{\underset{\text{CH}_3 \cdot \text{C} \cdot \text{Br}}{\text{C}}}$, boils at 146—146·5° under 740 mm. pressure; excess of bromine converts it into crotonylene tetrabromide, $\text{CBr}_2\text{Me} \cdot \text{CBr}_2\text{Me}$, which melts at 243°, and not at 230° as stated by Faworsky. Centro-symmetrical crotonylene dibromide, $\text{CH}_3 \cdot \overset{\text{CH}_3 \cdot \text{C} \cdot \text{Br}}{\underset{\text{Br} \cdot \text{C} \cdot \text{CH}_3}{\text{C}}}$, prepared by the action of zinc dust on the alcoholic solution of the tetrabromide, boils at 149—150°.

M. O. F.

Geometrically Isomeric Symmetrical Dimethylethylenes [ψ -Butylenes] from Tiglic and Angelic Acids. By JOHANNES WISLICENUS, HENRY PAUL TALBOT, and MARTIN HENZE (*Annalen*, 1900, 313, 228—242).—The hydriodides of tiglic and angelic acids (E. Schmidt, Abstr., 1881, 1126) are best prepared in chloroform solution, the former crystallising from light petroleum in colourless leaflets which melt at 86·5—87°; the hydriodide of angelic acid is more readily soluble than the isomeride melting at 59·5—60·5°, and undergoes transformation into the latter on repeated recrystallisation.

When the hydriodide of tiglic acid is treated with sodium carbonate, and the hydrocarbon which is generated collected in bromine, the dibromide which is formed yields bromo- ψ -butylene, $\text{CH}_3 \cdot \overset{\text{CH}_3 \cdot \text{C} \cdot \text{H}}{\underset{\text{Br} \cdot \text{C} \cdot \text{CH}_3}{\text{C}}}$, on treatment with alcoholic potash; when submitted to the same series of

changes, the hydriodide of angelic acid yields crotonylene hydrobromide, $\text{CH}_3 \cdot \overset{\text{H}}{\underset{\text{H}}{\text{C}}} \cdot \text{H}$
 $\text{CH}_3 \cdot \overset{\text{H}}{\underset{\text{H}}{\text{C}}} \cdot \text{Br}$. The former substance, which must have arisen from plano-

symmetrical ψ -butylene, $\text{CH}_3 \cdot \overset{\text{H}}{\underset{\text{H}}{\text{C}}} \cdot \text{H}$, boils at 93.5° , and is identical with the substance previously regarded as centro-symmetrical bromo- ψ -butylene (see preceding abstract), whilst crotonylene hydrobromide, boiling at $85-86^\circ$, is derived from centro-symmetrical ψ -butylene.

M. O. F.

Action of Bromine on Trimethylene under different Conditions. By GABRIEL GUSTAVSON (*J. pr. Chem.*, 1900, [ii], 62, 273-295).—A detailed description of researches, of which a summary has already appeared (Abstr., 1900, i, 535).

R. H. P.

Decomposition of Iodoform in Chloroform Solution. By M. C. SCHUYTEN (*Chem. Centr.*, 1900, ii, 1007; from *Bull. Acad. roy. Belg.*, [iii], 38, 625-639).—(1) In solutions of the same concentration, at the same temperature and with free access to air, the less the quantity of iodoform the greater the proportion decomposed. (2) In solutions of different concentrations, the greatest decomposition occurs in the most dilute. (3) The higher the temperature, the greater the decomposition. (4) As the volume of air in contact with the solution is increased, the amount of decomposition also increases. When air is excluded and the solution exposed to light, the greater the intensity of the light, the greater the decomposition effected. Solutions may be kept in the dark for a week without change, for under such conditions only a rise of temperature causes a separation of iodine. When a solution which has been exposed to light until iodine has begun to be liberated is placed in the dark, the decomposition still proceeds. A series of experiments, in which solutions were allowed to remain in contact with less air than that theoretically required for the separation of the whole of the iodine, showed that, nevertheless, the iodoform would in time be completely decomposed.

E. W. W.

isoNitroso-compounds. By ARNOLD F. HOLLEMAN (*Ber.*, 1900, 33, 2913-2914).—A question of priority (compare Abstr., 1896, i, 148; 1897, i, 599; Hantzsch and Schultze, Abstr., 1896, i, 353; Hantzsch and Veit, Abstr., 1899, i, 401; and Hantzsch, *Ber.*, 1900, 33, 2542).

A. H.

Acetals of Polyhydric Alcohols. By MARCEL DELÉPINE (*Compt. rend.*, 1900, 131, 745-747).—The diacetal of *i*-erythritol, which has not hitherto been described, is obtained by adding acetaldehyde to a cooled solution of *i*-erythritol in hydrochloric acid; it is soluble in chloroform, alcohol, or water, from which it crystallises in prismatic needles, melts at $94.5-95^\circ$, boils at 201° , and sublimes below the latter temperature. The following thermochemical data were obtained:

| | Molecular heat of combustion. | | Molecular heat of formation. |
|---------------------------------|-------------------------------|--------------------|------------------------------|
| | Constant volume. | Constant pressure. | |
| Glycol formal | 409·4 Cal. | 409·6 Cal. | 80·3 Cal. |
| „ acetal..... | 558·24 | 558·8 | 94·4 |
| <i>i</i> -Erythritol diformal.. | 744·3 | 744·6 | 166·2 |
| „ diacetal... | 1048·0 | 1048·8 | 188·6 |
| <i>d</i> -Mannitol triformal.. | 1083·22 | 1083·5 | 248·2 |
| „ triacetal .. | 1536·91 | 1538·1 | 283·5 |

These results show that the heat of formation increases with the number of hydroxyl groups in the alcohol, and is greater for the acetals than for the corresponding formals, conclusions which are in accord with the known facts respecting the relative stability of the compounds. N. L.

Geometrically Isomeric α -Methyl- β -crotonic Acids. By JOHANNES WISLICENUS and MARTIN HENZE (*Annalen*, 1900, 313, 243—250).—According to theoretical views expressed by J. Wislicenus, it was to be expected that the dibromide of angelic acid, $\text{CH}_3 \cdot \underset{\text{H}}{\underset{|}{\text{C}}} \cdot \text{H}$ $\text{Br} \cdot \underset{\text{C}}{\underset{|}{\text{C}}} \cdot \text{CH}_3$, would yield β -bromotiglic acid, $\text{CH}_3 \cdot \underset{\text{H}}{\underset{|}{\text{C}}} \cdot \text{CO}_2\text{H}$, on treatment with alcoholic potash, and that the dibromide of tiglic acid, $\text{H} \cdot \underset{\text{C}}{\underset{|}{\text{C}}} \cdot \text{CH}_3$ $\text{CH}_3 \cdot \underset{\text{C}}{\underset{|}{\text{C}}} \cdot \text{Br}$, would give rise to β -bromoangelic acid, $\text{CH}_3 \cdot \underset{\text{H}}{\underset{|}{\text{C}}} \cdot \text{CO}_2\text{H}$; of these, it might be anticipated that the former would be more stable than the latter, the salts of which should easily break up into metallic bromide, carbon dioxide, and crotonylene (dimethylacetylene). These anticipations have been verified.

β -Bromoangelic acid crystallises from light petroleum in rosette-like aggregates of needles melting at 94—95°; the sodium salt decomposes in aqueous solution, yielding crotonylene.

β -Bromotiglic acid crystallises from light petroleum in large, monoclinic prisms and melts at 100—101°. M. O. F.

Direct Nitration in the Fatty Series. By LOUIS BOUVEAULT and A. WAHL (*Compt. rend.*, 1900, 131, 687—689).—The action of well cooled fuming nitric acid on ethyl dimethylacrylate yields *ethyl nitrodimethylacrylate*, a pale yellow liquid of sp. gr. 1·1384 at 0°, with a peculiar piquant and somewhat disagreeable odour. It boils without decomposing at about 220° under atmospheric pressure. When dissolved in benzene, its molecular weight is normal. It is insoluble in water and acid, and dissolves slowly in cold solutions of alkali hydroxides, but is dissolved and decomposed on heating. Ordinary reducing agents have no action on it. When treated with alcoholic potash, it yields a potassium salt, $\text{C}_7\text{H}_{10}\text{O}_4\text{NK}$, from which, by the action of hydrochloric acid, an isomeric ethyl β -nitrodimethylacrylate is obtained as a colourless liquid which boils at 104—105° under 170 mm. pressure, has a sp. gr. 1·1279 at 0°/0°, and dissolves at once in cold solutions of alkali hydroxides. C. H. B.

Constitution of the Nitro-derivatives of Ethyl Dimethylacrylate. Ethyl Nitroacetate. By LOUIS BOUVEAULT and A. WAHL (*Compt. rend.*, 1900, 131, 748—750).—Ethyl dimethylacrylate is converted by the action of fuming nitric acid into ethyl α -nitrodimethylacrylate which, when treated with alcoholic potash, yields the potassium salt of the isomeric ethyl β -nitrodimethylacrylate. When an ethereal solution of ethyl β -nitrodimethylacrylate is saturated with dry ammonia, an unstable ammonium salt is formed, whereas the α -ester, when similarly treated, is converted into acetone and an ammonium compound, $C_4H_{10}O_4N_2$, from which hydrochloric acid liberates ethyl nitroacetate. This ester is thus obtained as a colourless liquid boiling at 105—107° under 25 mm. pressure, and having a sp. gr. 1.226 at 0°/0°, which appears to be isomeric with the ethyl nitroacetate described by de Forcrand as boiling at 151—152°. It is concluded from these results that ethyl α - and β -nitrodimethylacrylates have the constitutions $CM_e_2:C(NO_2)\cdot CO_2Et$ and $CH_2:CM_e\cdot CH(NO_2)\cdot CO_2Et$ respectively. N. L.

Oxidation of Higher Unsaturated Fatty Acids with Sulphuric Acid and Ammonium Persulphate. By ALEXIUS ALBITZKY (*Ber.*, 1900, 33, 2909—2910).—When oxidised with a mixture of sulphuric acid and ammonium persulphate, oleic, elaidic, erucic, and brassic acids give the dihydroxy-acids which have already been described as oxidation products when alkaline permanganate was used (compare Abstr., 1899, i, 862). T. M. L.

The two Campholytic Acids and Lauronolic Acid. By FERDINAND TIEMANN (*Ber.*, 1900, 33, 2935—2952).—[With MAX KERSCHBAUM and HERMANN TIGGES].—Liquid campholytic acid, $C_9H_{14}O_2$, first obtained by Walker as a product of the electrolysis of sodium orthoethyl camphorate (*Trans.*, 1893, 63, 498), and subsequently by Noyes from β -camphoramic acid, has been distinguished by the latter investigator as *cis-trans*-campholytic acid, the solid isomeride originally called *isolauronolic acid* being regarded as the *cis*-modification. By way of avoiding confusion, the authors refer to these compounds in the present paper as α - and β -campholytic acids respectively.

α -Campholytic acid, $C_9H_{14}O_2$, obtained from β -camphoramic acid by oxidation with sodium hypobromite, and subsequent treatment of the resulting aminodihydrocampholytic acid with nitrous acid, is separated from the accompanying hydroxydihydrocampholytic acid (Noyes, Abstr., 1895, i, 295) by agitation with light petroleum, which removes also the lactone, $C_9H_{14}O_2$; it is a colourless oil which becomes yellow on standing, boils at 126—128°, 139—140°, and 235—236° under pressures of 8 mm., 15 mm., and 760 mm. respectively, has a sp. gr. 1.014 at 17°, n_D 1.47116, and $[\alpha]_D$ -73 at 45°. *Campholytolactone*, $C_9H_{14}O_2$, distils readily in steam, forming a camphor-like mass with a peculiar odour; it melts at 115—116°, and boils at 105—108°, and 228—230° under pressures of 8 mm., and 760 mm. respectively. The *hydroxy-acid*, $C_9H_{16}O_3$, obtained by hydrolysing the lactone with baryta, crystallises from ethyl acetate in broad needles melting at 121°; in every respect but melting point it resembles hydroxydihydrocampholytic acid, passing readily into *isolauronolic acid* on treatment

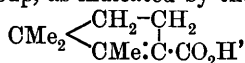
with acids, and the authors consider it probable that the relation between the two substances is one of geometrical isomerism, and that the hydroxyl group occupies the γ - instead of the β -position, as supposed by Noyes.

When α -campholytic acid is oxidised with alkaline potassium permanganate at 0° , two crystalline substances are produced, of which the *acid*, $C_9H_{14}O_4$, which crystallises from ethyl acetate in prisms melting and decomposing at 192° , is regarded by the authors as the hydroxyketonic compound, $CMe_2 \begin{matrix} \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \\ \text{CMe}(\text{OH}) - \text{CO} \end{matrix}$; this acid yields

no precipitate with copper acetate, whilst *dihydroxydihydrocampholytic acid*, $C_9H_{16}O_4$, which crystallises from ethyl acetate in octahedra, and melts at 158° , forms a crystalline copper salt. Oxidation with dilute nitric acid resolves α -campholytic acid into dimethyltricarballic and dimethylglutaric acids; the authors represent its constitution therefore by the formula $CMe_2 \begin{matrix} \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \\ \text{CMe} = \text{CH} \end{matrix}$, which accords with the

production of dimethyltricarballic acid, regarding the dimethylglutaric acid as due to the *isolaunonic acid* formed by molecular transformation preceding oxidation. β -Campholytic (*isolaunonic*) acid, when oxidised with potassium permanganate, yields *isocampholytonic* (*isolaunonic*) acid, along with dimethylhexanoic and dimethylglutaric acids, whilst dilute nitric acid produces dimethylglutaric and dimethylsuccinic acids, but no trace of dimethyltricarballic acid.

In consequence of these observations, the authors maintain that α -campholytic and *isolaunonic* acids are not geometrical isomerides, and that during the transformation into *isolaunonic* acid the change which α -campholytic acid undergoes is very profound, involving migration of the carboxyl group, as indicated by the formula,



for *isolaunonic* acid.

In the way that β -camphoric acid yields campholytic acid, launonic acid is obtained from α -camphoric acid, and because it differs slightly from the acid produced by Aschan's modification of the method of Fittig and Woring, which depends on the decomposition of bromocamphoric anhydride with alkali carbonate, has been called γ -launonic acid by Noyes. γ -Launonic acid, which is identical with the *allocampholytic* acid of Walker and Henderson (*Trans.*, 1895, **67**, 341), is a pale yellow oil which boils at 130 — 132.5° under 12 mm. pressure, has a sp. gr. 1.0177, n_D 1.47155, and $[\alpha]_D +145.9^\circ$ at 20° ; as, however, this value is not always observed, but varies between 118° and 146° , it is possible that the acid from this source is a mixture of two modifications having different optical properties. The acid from camphoric acid has α_D varying between 110° and 188° , bromocamphoric anhydride yielding launonic acid with the constant rotation $+199^\circ$ in a 1 dm. tube. Boiling acids convert launonic acid into campholactone, which melts at 50°

and yields hydroxydihydrolaunonic acid, $CMe_2 \begin{matrix} \text{CH}(\text{OH}) \cdot \text{CH}_2 \\ \text{CHMe} - \text{CH} \cdot \text{CO}_2\text{H}' \end{matrix}$ on hydrolysis; this crystallises from water in prisms melting at

144—145°, and when boiled in a vacuum yields campholactone, water, and an acid which melts at 189°. *Dibromodihydrolauronic acid*, $C_9H_{14}O_2Br_2$, produced in association with the bromolactone when the calculated amount of bromine acts on γ -lauronic acid in chloroform solution, crystallises from benzene and melts at 185°; the solution in dilute sodium carbonate rapidly deposits bromocampholactone, which melts at 187°. Laurolene (compare Walker and Henderson, *Trans.*, 1896, **69**, 750) boils at 121—122°, has sp. gr. 0.8008 at 17.5°, n_D 1.44376, and α_D +19.9° in a 1 dm. tube.

When lauronic acid is oxidised with potassium permanganate, a ketone and a dihydroxy-acid are produced. *Laurenone*, $C_8H_{12}O$, the ketone, is optically inactive, and forms a colourless liquid with a nutty odour; it boils at 92—95° under 16 mm. pressure, has a sp. gr. 0.9572 at 12.5°, and n_D 1.48535. The *oxime*, $C_8H_{13}ON$, crystallises from petroleum in prisms, and melts at 105—107°; the *hydroxylamino-oxime*, $C_8H_{16}O_2N_2$, forms white crystals melting at 159°, and when boiled with water and mercuric oxide develops a blue coloration, indicating the tertiary character of the hydroxylamine group.

Dihydroxydihydrolauronic acid, $C_9H_{16}O_4$, crystallises from water and melts at 153—154°; the *copper* salt is sparingly soluble.

M. O. F.

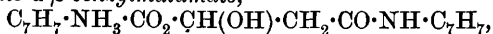
Oxalates. By GRÉGOIRE N. WYROUBOFF (*Chem. Centr.*, 1900, ii, 839—843; from *Bull. Soc. franç. Min.*, **23**, 65—141).—A detailed account of the double oxalates, $M'''_2(C_2O_4)_6M'_6$ where $M''' = Al, Cr, Fe$ and $M' = NH_4, K, Rb, Tl, Na, Li$. Some salts are also described containing two of the alkali metals; most of these come under the general formula given, but a few are of the more complex type $M'''_8(C_2O_4)_{24}M'_{24}$. The crystallography of the salts is described.

E. W. W.

Action of Ammonia and Amines on Halogen-succinic Acids. By OSKAR LUTZ (*Chem. Centr.*, 1900, ii, 1009—1014; from *Diss. Rostock*, 1899).—*d*- β -*Malamic acid*, $CO_2H \cdot CH(OH) \cdot CH_2 \cdot CO \cdot NH_2$, prepared by the action of ammonia on *l*-bromosuccinic acid, melts at 149°, has a sp. gr. 1.577 at 18°/4° and $[\alpha]_D$ 9.70° in aqueous solution; 100 parts of water dissolve 7.52 of the acid at 18°. The *silver* salt, $C_4H_6O_4NaAg$, forms lustrous leaflets and has $[\alpha]_D$ +16.4° in aqueous solution and dissociation coefficient $K = 0.0286$. *l*- β -*Malamic acid* is prepared from *d*-chlorosuccinic acid, from *l*-malamide, or from methyl hydrogen malate (see later); it melts at 148.5—149°, has a sp. gr. 1.576 at 18°/4°, $[\alpha]_D$ -9.33° in aqueous solution, and, like the dextro-acid, is readily hydrolysed by bases forming the corresponding malic acid. The *sodium* salt has $[\alpha]_D$ -27.32° in aqueous solution. *i*- β -*Malamic acid* is prepared from *i*-bromosuccinic acid, or by mixing equal quantities of the dextro- and lævo-acids, and may be separated into its components by means of the cinchonine salts; it melts at 148°, is almost insoluble in methyl or ethyl alcohol and insoluble in ether, and has a sp. gr. 1.526 at 18°/4°; 100 parts of water dissolve 4.02 of acid at 18°. *d*- β -*Cinchonine malamate* melts at 165—167°, and is less soluble in water than the corresponding lævo-compound. *i*- β -*Malamic acid* is not identical with Curtius and

Koch's acid (Abstr., 1887, 34), and attempts to obtain the latter by the method described by these authors failed, *i*- β -malic acid monamide being formed; hence a portion of the ester of diazosuccinamic acid must have the composition $\text{CO}_2\text{R}\cdot\text{CN}_2\cdot\text{CH}_2\cdot\text{CONH}_2$. Although the salts of β -malamic acid are not affected by heating in aqueous solution, the rotatory power of an aqueous solution of the acid increases on heating, whilst the acidity as determined by barium hydroxide solution decreases. Walden's rule (Abstr., 1896, i, 553) that of optical isomerides the one of higher melting point has a less solubility and a less molecular volume does not hold in the case of the β -malamic acids.

Benzylamine d- β -benzylmalamate,



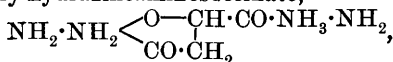
obtained by the action of benzylamine on *l*-bromosuccinic acid dissolved in methyl alcohol, melts at 152—153°, is soluble in water or methyl alcohol, and practically insoluble in ether, has $[\alpha]_D + 31\cdot43^\circ$ in methyl alcohol solution at 20° and $+ 28\cdot0^\circ$ in aqueous solution. *d- β -Benzylmalamic acid*, $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, obtained by the action of hydrochloric acid on the benzylamine salt, crystallises from light petroleum in lustrous leaflets, melts at 130—131°, is easily soluble in methyl or ethyl alcohol and insoluble in ether, has a sp. gr. 1·347 at 18°/4° and $[\alpha]_D + 13\cdot6^\circ$ in methyl alcohol solution; 100 parts of water dissolve 1·36 of the acid at 18°. The acid may also be prepared directly in aqueous solution. The sodium salt has $[\alpha]_D + 33\cdot8^\circ$ in aqueous solution. *l- β -Benzylamine benzylmalamate*, prepared from *d*-chlorosuccinic acid, has $[\alpha]_D - 31\cdot33^\circ$ in methyl alcohol solution. *l- β -Benzylmalamic acid* melts at 130—131°, has $[\alpha]_D - 13\cdot8^\circ$ in methyl alcohol solution, and sp. gr. 1·349 at 18°/4°; 100 parts of water dissolve 1·39 of the acid at 18°. *i- β -Benzylamine benzylmalamate*, obtained from *i*-bromosuccinic acid, melts at 149°, is soluble in water or methyl alcohol, insoluble in ether, and forms a silver salt, $\text{C}_{11}\text{H}_{12}\text{NO}_4\text{Ag}$. *i- β -Benzylmalamic acid* melts at 131°, and has a sp. gr. 1·360 at 18°/4°; 100 parts of water dissolve 0·820 of the acid at 18°. The acid may also be prepared by mixing the dextro- and lævo-acids, but in this case contraction does not occur (Liebisch, *Annalen*, 1895, 286, 140).

By the action of tribenzylamine on halogen succinic acids only inactive products are formed, but pyridine yields active compounds. The latter are extremely weak acids, and separate as such from alcoholic solutions since they do not combine with pyridine. Unlike the analogous triethylamine and isobutylamine compounds (Abstr., 1898, i, 127), the pyridine compounds, when hydrolysed by means of warm potassium hydroxide solution or hydrochloric acid, do not yield malic acid. *d-Pyridineaminosuccinic acid* [*d-Pyridiniummalic acid*], $\text{C}_5\text{NH}_5\cdot\text{O} > \text{CH}\cdot\text{CO}_2\text{H}$, obtained when a mixture of *l*-bromosuccinic acid and pyridine is left for two months, melts and decomposes at 190—191°, is easily soluble in hot water, alkalis or acids, insoluble in alcohol or ether, has a sp. gr. 1·435 at 18°/4°, and $[\alpha]_D + 10\cdot6^\circ$ when dissolved in 1 part of 2*N* hydrochloric acid solution and 4 parts of water; 100 parts of water dissolve 1·67 parts at 18°. The sodium

salt has $[\alpha]_D + 17.01$ in aqueous solution. The *silver* salt is very sensitive to the action of light. *l*- β -Pyridiniummalic acid, prepared by leaving a mixture of pyridine and *d*-chlorosuccinic acid for four months, melts at $190-191^\circ$, has a sp. gr. 1.435 at $18^\circ/4^\circ$, and $[\alpha]_D - 10.5^\circ$ when dissolved in $2N$ hydrochloric acid and 4 parts of water; 100 parts of water dissolve 1.435 of the acid at 18° . *i*- β -Pyridiniummalic acid, obtained from *i*-bromosuccinic acid, melts at $186-187^\circ$, and has a sp. gr. 1.435 at $18^\circ/4^\circ$; 100 parts of water dissolve 1.70 of the acid at 18° .

By the action of dibenzylamine on *l*-bromosuccinic acid, a product consisting of at least two isomerides is obtained, one of which is β -dibenzylmalamic acid, $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}(\text{C}_6\text{H}_5)_2$. Benzylmethylamine acts on *l*-bromosuccinic acid in a similar way.

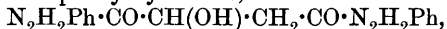
By the action of hydrazine on *l*-bromosuccinic acid, a compound which is probably hydrazineaminosuccinate,



or hydrazinehydrazomalamate,



is formed; it is easily soluble in water, insoluble in alcohol or ether, has $[\alpha]_D + 34.83^\circ$ in aqueous solution and when hydrolysed yields *d*-malic acid. Malic acid diphenylhydrazide,



prepared by the action of phenylhydrazine (3 mols.) on *l*-bromosuccinic acid (1 mol.) in alcoholic solution, melts at 214° and is identical with the compound obtained by the action of phenylhydrazine on ethyl malate and with Bülow's hydrazide (Abstr., 1887, 138) which melts at 213° ; 100 c.c. of absolute alcohol dissolve 0.0052 of this compound and 0.0070 of Bülow's hydrazide at 18° .

β -Malamic acid may also be obtained by partially hydrolysing malamide with hydrochloric acid or potassium hydroxide solution or by the action of ammonia on methyl hydrogen malate or ethyl malate. The increase in conductivity in the case of the sodium salt, $\mu_{1024} - \mu_{32} = 9.42$, indicates the monobasic character of the acid. Methyl *d*- β -malamate, $\text{CO}_2\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, melts at $75-76^\circ$, is soluble in hot methyl alcohol and has $[\alpha]_D + 12.7^\circ$ in methyl alcohol solution. *d*-Malamide, prepared from the preceding ester, melts at $156-157^\circ$, has $[\alpha]_D + 37.9^\circ$ in aqueous solution. Methyl *l*- β -malamate melts at $75-76^\circ$, and has $[\alpha]_D - 12.5^\circ$ in methyl alcohol solution. *l*-Malamide melts at $156-157^\circ$ and has $[\alpha]_D - 37.9^\circ$ in aqueous solution. Methyl *i*- β -malamate melts at 113° . *i*-Malamide melts at $163-164^\circ$.

Methyl *l*- α -malamate, $\text{CO}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}_2$, prepared by the action of dry ammonia on methyl malate, melts at $66-67^\circ$, is insoluble in ether and has $[\alpha]_D - 48.48^\circ$ in methyl alcohol solution. Ethyl *l*- α -malamate (Pasteur, Ann. Chim. Phys., 1853, [iii], 38, 457) melts at $102-103^\circ$, is soluble in alcohol but insoluble in ether and has $[\alpha]_D - 42.0^\circ$ in methyl alcohol solution. Malamide may be prepared from the esters of α malamic acid.

The ester prepared from β -malamic acid and that obtained from a dialkyl ester of malic acid yield the same diamide. The diamide

$\text{NH}_2 \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}(\text{C}_7\text{H}_7)$, prepared by the action of benzylamine on the ester of α -malamic acid, is identical with the compound prepared by the action of alcoholic ammonia on the ester of β -benzylmalamic acid but not with the mixed amide obtained by the action of ammonia on the methyl ester prepared from β -malamic acid by means of the silver salt. *Methyl d- β -benzylmalamate* melts at 105° , is easily soluble in hot alcohol, insoluble in ether and has $[\alpha]_D + 12.8^\circ$ in methyl alcohol solution.

d- β -Benzylmalamide, prepared by the action of alcoholic ammonia on the corresponding ester, melts at 131° , is easily soluble in methyl or ethyl alcohol or hot water, insoluble in ether, and has $[\alpha]_D + 42.40^\circ$ in methyl alcohol solution. *l- β -Benzylmalamide*, obtained by the action of benzylamine on methyl *l*- α -malamate, melts at 131 — 132° and has $[\alpha]_D - 42.62^\circ$ in methyl alcohol solution. *d- α -Benzylmalamide*, obtained by the action of benzylamine on methyl *d- β -malamate* in methyl alcohol solution, melts at 125 — 126° and has $[\alpha]_D + 44.56^\circ$ in methyl alcohol solution. *d- α -Benzylallylmalamide*,

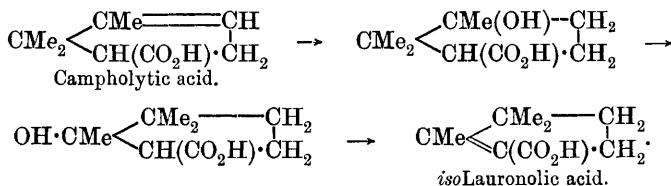
$\text{C}_3\text{H}_5 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, prepared from allylamine and methyl *d- β -benzylmalamate*, crystallises in needles, melts at 107 — 108° , is easily soluble in methyl or ethyl alcohol, and has $[\alpha]_D + 41.04^\circ$ in methyl alcohol solution. *d- α -Allylmalamide*, $\text{C}_3\text{H}_5 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, obtained from allylamine and methyl *d- β -malamate*, melts at 124 — 125° and has $[\alpha]_D + 49.68^\circ$ in methyl alcohol solution. *l- β -Allylmalamide*,

$\text{NH}_2 \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_3\text{H}_5$, prepared from methyl *l*- α -malamate and allylamine in alcoholic solution, melts at 134 — 135° , and has $[\alpha]_D - 52.25^\circ$ in methyl alcohol solution. *d- β -Benzylmethylmalamide*,

$\text{NHMe} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, obtained from methyl *d- β -benzylmalamate* and methylamine in alcoholic solution, melts at 128° and has $[\alpha]_D + 49.64^\circ$ in methyl alcohol solution.

The rotatory power of the preceding malic acid derivatives is less dependent on the size of the groups introduced than on their nature and position in the molecule. E. W. W.

Constitution of Camphoric Acid, and the Migrations which take place in its Molecule. By G. BLANC (*Compt. rend.*, 1900, 131, 803—806. Compare Abstr., 1899, i, 300, 536; 1900, i, 507; Trans., 1900, 77, 374, 1053).—The results obtained by the oxidation of inactive campholytic acid, prepared from *isolauronolic acid*, were found to be in agreement with those obtained by Tiemann from active campholytic acid (this vol., i, 5). A lactone (campholytolactone of Tiemann) melting at 114 — 115° was obtained, and, on oxidation, the campholytic acid was converted into dimethyltricarballic acid, melting at 156 — 157° . From these results, it follows that the constitution of campholytic acid is that which is given below. The conversion of campholytic acid into *isolauronolic acid* is readily explained, if it is assumed that 1 mol. H_2O is first taken up, then a methyl group and a hydroxyl group change position, and that, finally, 1 mol. H_2O is eliminated, thus;



The author concludes that Bouveault's formula for camphoric acid must be abandoned. H. R. LE S.

Compounds of Glycuronolactone. By G. GIEMSA (*Ber.*, 1900, 33, 2996—2998).—The *oxime* of glycuronolactone, $\text{C}_6\text{H}_9\text{O}_6\text{N}$, separates from alcohol in large, clear crystals, melts and decomposes at 149° and has $[\alpha]_D + 14.40^\circ$; the normal *potassium* salt has $[\alpha]_D + 11.73^\circ$.

The *semicarbazone*, $\text{C}_7\text{H}_{11}\text{O}_6\text{N}_3$, crystallises from hot water in long, white, silky needles, melts and decomposes at 188° , and has $[\alpha]_D - 20.83^\circ$.

The *phenylbenzylhydrazone*, $\text{C}_{19}\text{H}_{20}\text{O}_5\text{N}_2$, crystallises from alcohol in long, white, silky needles, and melts, with decomposition, at 141° ; the *potassium* salt crystallises in needles, melts at 176 — 178° , and has $[\alpha]_D - 20.29^\circ$.

The *bromophenylhydrazone*, $\text{C}_{12}\text{H}_{13}\text{O}_5\text{N}_2\text{Br}$, crystallises from alcohol in square tablets, and melts, with decomposition, at 142° ; the potassium salt is dextrorotatory.

The *phenylhydrazone*, $\text{C}_{12}\text{H}_{14}\text{O}_5\text{N}_2$, crystallises from alcohol in pale yellow needles, and melts at 160° . T. M. L.

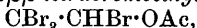
Bromal Acetate, Acetyl bromal Chloride and Bromide. By EMILIO GABUTTI (*Gazzetta*, 1900, 30, ii, 191—196. Compare Abstr., 1900, i, 370).—*Bromal diacetate* ($\beta\beta\beta$ -tribromoethylidene diacetate), $\text{CBr}_3\cdot\text{CH}(\text{OAc})_2$, obtained by the interaction of bromal and acetic anhydride, separates from ether in lozenge-shaped laminae, which melt at 76° , and are soluble in alcohol; on prolonged boiling with concentrated aqueous sodium hydroxide, it yields bromoform and sodium acetate and formate.

Acetyl bromal chloride (α -chloro- $\beta\beta\beta$ -tribromoethyl acetate),



prepared by the action of acetyl chloride on bromal, is obtained as an oil boiling at 45° with partial decomposition; it is very soluble in alcohol or ether, and with hot concentrated alkali hydroxide solution yields bromoform and the acetate, formate, and chloride of the alkali metal.

Acetyl bromal bromide ($\alpha\beta\beta\beta$ -tetrabromoethyl acetate),



is an oil boiling and decomposing at 75° ; it is readily soluble in alcohol or ether, and with alkali hydroxides yields products similar to those obtained from the corresponding chloride. T. H. P.

Derivatives of α -Nitro- β -dinitropropaldehyde. By JOSEPH TORREY, jun., and OTIS FISHER BLACK (*Amer. Chem. J.*, 1900, 24, 452—465).—By the action of potassium nitrite on muco-

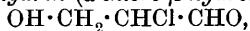
bromic acid, Hill and Sanger (Abstr., 1883, 47) obtained an orange-red salt, $C_3H_5O_7N_3K_2$. The authors find that this compound is the dipotassium salt of α -nitro- β -dinitropropionic acid; this view of its constitution was first suggested by the ease with which it is converted into the potassium salt of nitromalonaldehyde when heated with water or dilute alcohol (Hill and Torrey, Abstr., 1899, i, 788).

When this salt is treated with an ethereal solution of hydrogen chloride, $\alpha\beta$ -trinitropropaldehyde is obtained on evaporation as a colourless oil which, if left for a few minutes at the ordinary temperature, undergoes violent decomposition. The *anil* crystallises in light yellow needles and decomposes at 90° ; its *aniline*, *mono-* and *di-potassium*, and *barium* salts are described. The corresponding *p-tolil* and its *p-toluidine*, *mono-* and *di-potassium*, and *barium* salts were prepared. By the action of methylamine on the orange-red salt, the *monopotassium* salt of the methylimide of trinitropropionic acid is produced; when an aqueous solution of this salt is acidified with hydrochloric acid, the *methylimide* separates in white, pearly crystals; its *dipotassium* salt was also obtained. E. G.

Glyceraldehyde. By ALFRED WOHL and CARL NEUBERG (*Ber.*, 1900, 33, 3095—3110. Compare Abstr., 1898, i, 555, and 1900, i, 11).—Details of the preparation of glyceraldehyde from acraldehyde acetal are given. The aldehyde forms colourless, pointed needles or prisms which frequently form stellate aggregates, and, like carbohydrates in general, it is sparingly soluble in organic media, but dissolves somewhat readily in water. It may be removed from aqueous solution by means of lead acetate and ammonia, but the resulting white pulverulent precipitate, when suspended in water and decomposed with hydrogen sulphide, yields a liquid which does not reduce Fehling's solution.

Glyceraldehydophenylmethylhydrazone, $OH \cdot CH_2 \cdot CH(OH) \cdot CH : N_2 \cdot MePh$, crystallises from a mixture of benzene and light petroleum in colourless, shining leaflets or prismatic needles which melt at 120° , but after solidification the substance does not fuse below 220° , when it decomposes with evolution of gas. The *diphenylhydrazone*, $C_3H_5O_2 : N_2 \cdot Ph_2$, resembles the foregoing compound, and melts at 133° . The *p-bromophenyllosazone*, $OH \cdot CH_2 \cdot C(N_2H \cdot C_6H_4Br) \cdot CH : N_2H \cdot C_6H_4Br$, melts at 168° .

Glyceraldehyde chlorohydrin (α -chloro- β -hydroxypropaldehyde),



is prepared by the action of hypochlorous acid on acraldehyde acetal, the resulting acetate being hydrolysed by *N*/10 sulphuric acid; it distils with slight decomposition at 118° under a pressure of 30 mm. as a yellow, viscous liquid, and has an odour that is not unpleasant, although the vapour has a violent action on the mucous membrane. The *p-bromophenylhydrazone*, $C_3H_5OCl : N_2H \cdot C_6H_4Br$, separates from alcohol in slender, yellow needles melting at 61° .

When a dilute solution of glyceraldehyde and phloroglucinol is treated with a few drops of sulphuric acid, a gradual separation of colourless, pearly leaflets takes place, and is complete in about 10 hours. The new substance, $C_{15}H_{16}O_8$, is sparingly soluble in chloroform, benzene, ether, or hot water, but dissolves fairly readily in acetone, acetic

acid, and ethyl acetate. When heated, it turns orange at 200° , and is not melted at 280° . The solution of the substance in sodium hydroxide reduces warm Fehling's solution, and also ammoniacal solutions of mercury and silver. The formation of this compound occurs in very dilute solutions, and is characteristic of glyceraldehyde.

Glyceraldoxime, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{NOH}$, is a colourless, viscid liquid which is miscible with water, alcohol, or pyridine, but insoluble in ether. It gives a white precipitate with ammoniacal lead acetate in aqueous solution; the lead compound, $\text{C}_3\text{H}_7\text{O}_6\text{NPb}_3$, when heated turns yellow, and at a temperature slightly above 100° deflagrates, depositing small beads of metallic lead.

On heating the oxime with an equal weight of potassium hydroxide until effervescence occurs, and treating the hot mass with cold 50 per cent. acetic acid, glycolaldehyde is produced, and may be isolated in the form of its osazone, or one of the following new derivatives. *Glycolaldehyde diphenylosazone*, $\text{C}_2\text{H}_2(\text{N}\cdot\text{NPh}_2)_2$, forms light yellow needles melting at 207° , dissolves in warm acetic acid, producing an emerald-green solution, and imparts a dark violet coloration to sulphuric acid. *Glycolaldehyde p-nitrophenylosazone*, $\text{C}_2\text{H}_2(\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, crystallises from a mixture of pyridine and toluene in claret-coloured, glistening needles, and from hot benzonitrile in scarlet, stellate aggregates of needles, and melts at 311° ; it is nearly insoluble in the ordinary media, but dissolves readily in various nitrogenous organic liquids, including nitrobenzene, aniline, pyridine, and nitriles.

Under the influence of 1 per cent. aqueous potash at 0° , glyceraldehyde condenses to a hexose, which was identified as β -acrose.

A. L.

Solidification of Acetone. By CARLO FORMENTI (*L'Orosi*, 1900, 23, 223—224).—On placing acetone in a test-tube surrounded by liquid air it almost immediately begins to diminish in volume, and then becomes transformed into a snow-white mass of minute crystals which quickly liquefy when removed from the liquid air. No intermediate syrupy condition, such as occurs with alcohol, was observed in either change.

T. H. P.

Platinum-Carbon Compounds. By WILHELM PRANDTL and KARL A. HOFMANN (*Ber.*, 1900, 33, 2981—2983).—A compound, $\text{PtCl}_2\cdot\text{C}_6\text{H}_{10}\text{O}$, identical with the product obtained by Zeise (*J. pr. Chem.*, 1837, 20, 193) from platinic chloride and acetone, is formed by the action of mesityl oxide on a solution of chloroplatinic acid. When chloroform is boiled with chloroplatinic acid for several days, a product, $\text{PtCl}_2\cdot\text{C}_2\text{H}_4$, may be obtained, crystallising from toluene in pale yellow needles which begin to decompose at 140° .

J. J. S.

Methyl Nonyl Ketone. By HENRI CARETTE (*J. Pharm.*, 1900, [vi], 12, 217—222. Compare *Abstr.*, 1899, i, 860).—Benzaldehyde and methyl nonyl ketone react in presence of a 0.25 per cent. alcoholic solution of potassium hydroxide to yield a compound, $\text{C}_{18}\text{H}_{26}\text{O}$; this forms nacreous crystals, melts at 41 – 42° , boils at 245° under 35 mm., but decomposes at 200° under atmospheric pressure, and is very readily soluble in boiling alcohol, ether, glacial acetic acid, or benzene.

With a 1 per cent. solution of potassium hydroxide in 95 per cent. alcohol in the cold this compound is formed, together with a polymeride, $C_{36}H_{52}O_2$, melting at 116° . If, however, the mixture is boiled immediately after the addition of the potassium hydroxide, the compound melting at 116° is the sole product. This compound crystallises in aggregates of slender needles, which are soluble in alcohol, ether, glacial acetic acid, or benzene; it decomposes at 200° under atmospheric pressure, but boils and decomposes at 310° under 35 mm. It is also obtained when the compound melting at $41-42^\circ$ is boiled with a 1 per cent. solution of potassium hydroxide in 95 per cent. alcohol.

H. R. LE S.

Acetylœnanthylidene and Benzoylœnanthylidene [Acetyl and Benzoylheptinene] and their Conversion by Hydration into β -Diketones. By CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1900, 131, 710—712. Compare Abstr., 1900, i, 20, 397).— *α -Acetylheptinene*, $CH_3Me \cdot [CH_2]_3 \cdot C:CAc$, produced by adding acetic chloride to the sodium derivative of heptinene suspended in ether, is a liquid with a pungent odour; it boils at $91-93^\circ$ under 18 mm. pressure, has a sp. gr. 0.8819 at 0° and n_D 1.4453 at 24° .

Acetylhexoxylmethane, $CH_3Me \cdot [CH_2]_4 \cdot CO \cdot CH_2Ac$, obtained by hydrating the preceding compound through the agency of sulphuric acid, is a colourless liquid boiling at $105-107^\circ$ under 22 mm. pressure, and has a sp. gr. 0.9378 at 0° ; it solidifies at -23° and melts at -18° .

α -Benzoylheptinene, $CH_3Me \cdot [CH_2]_3 \cdot C:CBz$, prepared in a similar manner to the corresponding acetyl derivative, boils at $177-179^\circ$ under 19 mm. pressure, solidifies at -23° and melts at -5° .

Benzoylhexoxylmethane, $CH_3Me \cdot [CH_2]_4 \cdot CO \cdot CH_2Bz$, formed by the action of sulphuric acid on the preceding substance, boils at $185-186^\circ$ under 18 mm. pressure.

These diketones give the reactions characteristic of β -diketones; they yield blue copper salts soluble in chloroform, develop red colorations with alcoholic solutions of ferric chloride, and are decomposed by alkalis.

G. T. M.

Decomposition of Ketones of Acetylenic Function by means of Alkalis. By CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1900, 131, 800—803. Compare Abstr., 1900, i, 397).—An aqueous solution of potassium hydroxide has no action on α -acetylheptylinene or α -benzoylheptylinene in the cold, but when boiling, it hydrolyses the former into methyl amyl ketone, acetone, hexoic acid, and acetic acid, and the latter into methyl amyl ketone, acetophenone, hexoic acid, and benzoic acid. These two decompositions are easily explained if it is assumed that, before hydrolysis takes place, a diketone is formed by the addition of a mol. of water.

H. R. LE S.

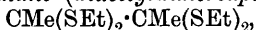
Disulphones. IV. Mercaptoles and Sulphones from Diketones. By THEODOR POSNER (*Ber.*, 1900, 33, 2983—2993. Compare Abstr., 1899, i, 604; 1900, i, 5, 16).— α -, β -, or γ -Diketones which contain both carbonyl groups attached to methyl radicles, for example, diacetyl, acetylacetone, acetonylacetone, readily react with 4 mols. of

a mercaptan, yielding dimercaptols, and these on oxidation yield tetrasulphones.

If, however, one of the carbonyl groups in an α - or β -diketone is attached to a substituted methyl group, as in acetylpropionyl, methylacetylacetone, or benzoylacetone, the ketone reacts with only 2 mols. of a mercaptan, yielding a ketomercaptol, which on oxidation gives a ketodisulphone. In the case of benzil, the condensation only occurs in the presence of zinc chloride, and then the product is a ketomercaptol, which on oxidation is converted back into its constituents. γ -Diketones always yield dimercaptols, and these on oxidation form tetrasulphones.

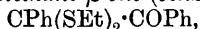
Similar reactions are met with in substituted ethyl acetoacetates.

$\beta\beta\gamma\gamma$ -Tetraethylthiolbutane (diacetyldimercaptol),



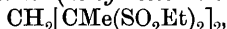
on oxidation with cold saturated potassium permanganate, yields the corresponding tetrasulphone, $\text{C}_2\text{Me}_2(\text{SO}_2\text{Et})_4$, which crystallises from alcohol in large prisms melting at $76-81^\circ$ (corr.). $\beta\beta$ -Diethylsulphonepentane- γ -one (acetylpropionyl disulphone), $\text{CMe}(\text{SO}_2\text{Et})_2 \cdot \text{COEt}$, crystallises in rhombic plates melting at $48-49^\circ$. Acetylisobutyryl disulphone ($\beta\beta$ -diethylsulphone- δ -methylpentane- γ -one), crystallises in colourless plates melting at $81-82^\circ$.

$\alpha\beta$ -Diphenyl- α -diethylthiolethane- β -one (benzilmercaptol),

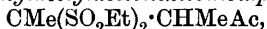


forms monoclinic crystals melting at $59.5-60^\circ$. By the condensation of benzoin with ethyl mercaptan in the presence of hydrogen and zinc chlorides, a substance, $\text{C}_{18}\text{H}_{20}\text{S}_2$, the constitution of which has not been determined, is obtained.

$\beta\beta\gamma\gamma$ -Tetraethylthiolpentane (acetylacetone tetrasulphone),



forms thick, rounded crystals melting at 111° . β -Diethylsulphone- γ -methylpentane- δ -one (methylacetylacetone ketodisulphone),

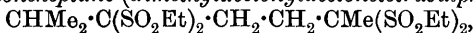


crystallises in colourless plates melting at $122-123^\circ$.

α -Phenyl- γ -diethylsulphonbutane- α -one (benzoylacetone ketodisulphone),

$\text{COPh} \cdot \text{CH}_2 \cdot \text{CMe}(\text{SO}_2\text{Et})_2$, crystallises in colourless plates melting at $109-111^\circ$.

$\beta\beta\epsilon\epsilon$ -Tetraethylsulphonehexane, $\text{C}_2\text{H}_4[\text{CMe}(\text{SO}_2\text{Et})_2]_2$, crystallises from acetic acid in iridescent plates melting at $200-201^\circ$. β -Methyl- $\gamma\gamma\zeta\zeta$ -tetraethylsulphoneheptane (dimethylacetonylacetone tetrasulphone),



forms a crystalline powder melting at $129-131^\circ$.

The ketodisulphone derivatives which contain a free carbonyl group do not react with hydroxylamine, phenylhydrazine, or semicarbazide.

J. J. S.

Carbohydrates of Carageen Moss. By J. ŠEBOR (*Chem. Centr.*, 1900, ii, 846-847; from *Oesterr. Chem.-Zeit.*, 3, 441-444).—The alga *Chondrus crispus*, from which the mucilage was prepared, on oxidation yielded 23.4 per cent. of mucic acid corresponding with 29.6 of galactose and when distilled with a 12 per cent. solution of hydrochloric acid gave 1.2 per cent. of furfuraldehyde corresponding with 2.5 of

pentosans. By extracting the moss with water and precipitating with alcohol, the mucilage is obtained as an amorphous, yellowish-brown powder, which swells when immersed in water, and becomes brown when treated with iodine. The cells of the algæ also contain proteids and salts. The dry jelly free from ash yields 41.9 per cent. of galactose (= 37.8 of galactan) and 4.1 of pentoses (= 3.6 of pentosans). In the product obtained by treating the algæ with a 0.5 per cent. solution of sulphuric acid, galactose, dextrose, and lævulose were detected but neither arabinose nor xylose. The mucilage appears to be a complex carbohydrate formed from galactose, dextrose, and lævulose or a mixture of galactan with glucosan and lævulosan, and a small quantity of a pentosan which is probably xylan; the sugars are not present, however, in the proportions contained in raffinose. The carbohydrate has probably a large molecular weight and like starch serves as a store of nutriment for the plant.

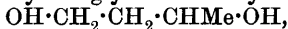
E. W. W.

Cellulose, Hydrocellulose, Mercerised and Precipitated Cellulose. By LÉO VIGNON (*Compt. rend.*, 1900, 131, 708—709. Compare Bumcke and Wolfenstein, *Abstr.*, 1899, i, 852).—The properties of cotton cellulose, hydrocellulose, mercerised and precipitated cellulose differ markedly from those of oxycellulose; for example, the former substances have no reducing action on solutions of copper salts and furnish far smaller quantities of sugar when heated for six hours with dilute hydrochloric acid, cellulose and its derivatives yielding from 3.3 to 4.4 per cent. of reducing sugar, whereas oxycellulose gives rise to 14.7 per cent. of this product.

The heats of combustion of cellulose, hydrocellulose, mercerised cellulose and precipitated cellulose are 4223, 4006, 3980, and 3982 cal. respectively. The concentrated solutions of alkalis employed in mercerising cotton and the dilute acids used in forming Girard's hydrocellulose, hydrate and probably depolymerise cellulose without conferring on the substance any new chemical properties. Oxycellulose, on the other hand, cannot exist in concentrated alkaline solutions as it breaks up into cellulose and a soluble acid, behaving under these conditions like furfuraldehyde which yields furfurylic alcohol and pyromucic acid.

G. T. M.

Amino-alcohols. By LOUIS HENRY (*Chem. Centr.*, 1900, ii, 1008—1009; from *Bull. Acad. roy. Belg.*, 38, 584—606).— γ -Aminobutyl alcohol, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, prepared by the action of sodium on an alcoholic solution of β -cyanopropyl alcohol, is a colourless liquid, boils at 125° and 206° under pressures of 34 and 776 mm. respectively, is soluble in alcohol but insoluble in ether, has a sp. gr. 0.967 at 12°, and dissolves in water with development of heat, forming a hydrate. The *dibenzoyl* derivative, $\text{NH} \cdot \text{Bz} \cdot \text{C}_6\text{H}_5 \cdot \text{OBz}$, crystallises in needles and melts at 58°. By the action of nitrous acid on aminobutyl alcohol, tetramethylene glycol and butylene glycol,



are formed, and by the action of formaldehyde, the compound $\text{OH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_4\text{H}_8 \cdot \text{OH}$ is obtained.

Aminoisopropyl alcohol, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH}$, prepared by reducing

the corresponding nitro-compound with iron and acetic acid, boils at 160° under 750 mm. pressure.

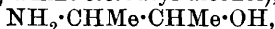
When groups, such as OH, Cl, NO_2 , are replaced by the amino-group in compounds containing two or three carbon atoms, the boiling point of the product is always high when an aminoalcohol, $\text{X}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NH}_2$, is formed. This is explained by assuming a reaction to occur between the OH and the NH_2 group, a theory which derives support from the fact that heat is developed when liquid amines, such as diethylamine, *isobutylamine*, *isoamylamine*, or piperidine, are dissolved in methyl or ethyl alcohol, whilst their solution in ethyl acetate or ether is not attended by any development of heat. The aminoalcohols of the types $\text{OH}\cdot\text{CH}_2\cdot\text{NR}_2$ or $\text{OH}\cdot\text{C}\cdot\text{C}\cdot\text{NH}_2$ combine with hydrogen cyanide, amines, or aliphatic nitro-compounds, with elimination of water, to form compounds such as $\text{CN}\cdot\text{CH}_2\cdot\text{NMe}_2$, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{NMe}_2$, or $\text{NO}_2\cdot\text{C}(\text{CH}_2\cdot\text{C}_5\text{NH}_{10})_3$, but aminobutyl alcohol does not give these reactions.

Since the oxide, $\text{CH}_2\begin{smallmatrix} \text{CHMe} \\ \text{CHMe} \end{smallmatrix}\text{O}$, unlike ethylene oxide, is incapable of acting on ammonia or amines, probably trimethylene oxide, $\text{CH}_2\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\text{O}$, would behave in this respect like the former.

E. W. W.

2:1-Aminopropanol and 2:3-Aminobutanol. By EDUARD STRAUSS (*Ber.*, 1900, **33**, 2825—2830).—2:1-Aminopropanol (aminoisopropyl alcohol), $\text{NH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, is produced when an aqueous solution of isonitrosoacetone is treated with successive small quantities of sodium amalgam and hydrochloric acid, and is isolated by evaporating to dryness, and distilling the residue with potassium hydroxide. It boils at 156 — 158° under atmospheric pressure, and when heated at 100° with fuming hydrobromic acid yields β -bromopropylamine. The *platinichloride*, $(\text{C}_3\text{H}_9\text{ON})_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in yellow leaflets melting at 200° . β -Hydroxypropylphenylthiocarbamide, $\text{C}_3\text{H}_7\text{O}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, forms needles melting at 106.5° .

2:3-Aminobutanol (γ -amino-*sec.* butyl alcohol),



from isonitrosomethyl ethyl ketone, boils at 155 — 158° under atmospheric pressure. The *platinichloride*, $(\text{C}_4\text{H}_{11}\text{ON})_2\cdot\text{H}_2\text{PtCl}_6$, forms orange leaflets which melt at 185° .

Phenyl- β -hydroxybutylthiocarbamide, $\text{C}_4\text{H}_9\text{O}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, crystallises in hard, white needles melting at 76 — 78° . When heated with strong hydrobromic acid, it is converted into N-phenylbutylene- ψ -thiocarbamide, $\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{S}—\text{CHMe} \\ \text{NH}\cdot\text{CHMe} \end{smallmatrix}$, which crystallises in needles melting at 114° and gives a *picrate*, $\text{C}_{11}\text{H}_{14}\text{N}_2\text{S}\cdot\text{C}_6\text{H}_5\text{O}_7\text{N}_3$, melting at 186° .

β -Bromoaminobutane, $\text{CHMeBr}\cdot\text{CHMe}\cdot\text{NH}_2$, was isolated in the form of its *picrate*, $\text{C}_4\text{H}_{10}\text{NBr}\cdot\text{C}_6\text{H}_5\text{O}_7\text{N}_3$, which crystallises from water in yellow needles melting at 165 — 166° .

Butylene- ψ thiocarbamide, $\text{NH}\cdot\text{C}\begin{smallmatrix} \text{S}—\text{CHMe} \\ \text{NH}\cdot\text{CHMe} \end{smallmatrix}$, is a brownish oil,

and gives a *picrate*, $C_5H_{10}N_2S, C_6H_3O_7N_3$, crystallising in prisms and melting at $199-200^\circ$, and a *platinichloride*, $(C_5H_{10}N_2S)_2, H_2PtCl_6$, crystallising in tablets and melting at $188-195^\circ$.

2-Phenyl-4:5-dimethyloxazoline, $CPh \begin{smallmatrix} O \cdot CHMe \\ \diagdown \\ N \cdot CHMe \end{smallmatrix}$, was obtained as a yellowish oil. The *platinichloride*, $(C_{11}H_{13}ON)_2, H_2PtCl_6$, forms leaflets melting at 193.5° , and the *picrate*, $C_{11}H_{13}ON, C_6H_3O_7N_3$, needles melting at 133° .

2-Phenyl-4:5-dimethylthiazoline, $CPh \begin{smallmatrix} S \cdot CHMe \\ \diagdown \\ N \cdot CHMe \end{smallmatrix}$, forms a yellow oil. The *platinichloride*, $(C_{11}H_{13}NS)_2, H_2PtCl_6$, crystallises in bright red needles melting and decomposing at $179-180^\circ$, and the *picrate*, $C_{11}H_{13}NS, C_6H_3O_7N_3$, in yellow leaflets melting at $164-165^\circ$.

2-Mercapto-4:5-dimethylthiazoline separates from water in beautiful needles melting at $53-58^\circ$. A. L.

Action of Halogens on Ethyl Sodiocyanoacetate. By GIORGIO ERRERA and F. PERCIABOSCO (*Ber.*, 1900, 33, 2976-2981. Compare Thorpe and Young, *Trans.*, 1900, 77, 936).—The reaction between iodine or bromine and ethyl sodiocyanoacetate proceeds best in ethereal solution, the chief product being *ethyl tricyanotrimethylenetricarboxylate*, $CO_2Et \cdot \begin{smallmatrix} C(CN) \\ | \\ C(CN) \end{smallmatrix} > C(CN) \cdot CO_2Et$, which crystallises from dilute alcohol in needles or flat crystals melting at 119° ; it is probably identical with the substance described by Thorpe and Young as ethyl dicyanosuccinate, which melts at 120° . Various other products have been isolated, but have not yet been investigated. Alkalis readily hydrolyse the ester; when barium hydroxide is employed, the product is trimethylenetetra-carboxylic acid, melting at $193-194^\circ$ (*Abstr.*, 1885, 1125, and 1895, i, 269); when heated at 200° , this acid yields trimethylenetricarboxylic acid, melting at 215° . When cold dilute barium hydroxide solution is employed for the hydrolysis, the products are *tricyanotrimethylene*, $\begin{smallmatrix} CN \cdot CH \\ | \\ CN \cdot CH \end{smallmatrix} > CH \cdot CN$, melting at $182-184^\circ$, and *cyanotrimethylenetricarboxylic acid*, $CO_2Et \cdot \begin{smallmatrix} CH \\ | \\ CN \end{smallmatrix} > C(CN) \cdot CO_2H$, melting and decomposing at $194-195^\circ$.

J. J. S.

Peculiar Disruption of the Camphor Ring. By FERDINAND TIEMANN (*Ber.*, 1900, 33, 2953-2959).—[With GEORG LEMME and MAX KERSCHBAUM].—By the action of potassium or ammonium hydroxide on α -camphorisoimide hydrochloride, $C_8H_{14} \begin{smallmatrix} C(NH) \\ \diagdown \quad \diagup \\ CO \end{smallmatrix} > O, HCl$, Hoogewerff and van Dorp obtained cyanolauroic acid (*Abstr.*, 1896, i, 314), which melts at $151-152^\circ$; the authors have prepared this compound by the action of acetic anhydride on isonitrosocamphor, and call it α -camphornitrilic acid. β -Camphorisoimide hydrochloride yields the corresponding cyano-acid, which Hoogewerff and van Dorp called cyanodihydrocampholytic acid (*loc. cit.*), and the authors, β -camphor-

nitrilic acid. Expecting that distillation of the calcium salts would convert these substances into the nitriles of α -campholytic and lauronolic acids respectively, the present investigators have discovered that a more profound change takes place, both compounds yielding α -dimethylheptenonitrile, which is oxidised by potassium permanganate to acetone, methylglutaric acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, and methylsuccinic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. A disruption of the camphor ring has thus taken place between the methylated and the dimethylated carbon atoms, and the production of the same nitrile from both acids can be explained only, in the authors' opinion, by the migration of a cyano-group. According to Bredt's camphor formula, β -camphornitrilic acid would be represented by the expression $\text{CMe}_2\begin{smallmatrix} \text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2 \\ \text{CMe}(\text{CN})-\text{CH}_2 \end{smallmatrix}$.

α -Dimethylheptenonitrile, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CN}$, boils at $92-95^\circ$ under 16 mm. pressure, has a sp. gr. 0.8563 at 17° , and $n_D 1.4486$. α -Dimethylheptenoic acid, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, boils at $140-141^\circ$ and $236-240^\circ$ under pressures of 18 mm. and 760 mm. respectively, has a sp. gr. 0.934 at 17° , and $n_D 1.4501$; the *amide* crystallises from benzene and melts at 84° . M. O. F.

Constitution of β -Camphornitrilic Acid. By FERDINAND TIEMANN (*Ber.*, 1900, 33, 2960—2965).—[With HERMANN TIGGES].—In the case of α -camphornitrilic acid it can be shown that it is the nitrile corresponding with α -camphoramie acid by partial hydrolysis to this substance, but β -camphornitrilic acid does not undergo this change. In order to prove that it corresponds with β -camphoramie acid, it has been converted into the amide, $(\beta)\text{CN}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NH}_2(\alpha)$, which was then oxidised with sodium hypobromite to the nitrile of amino[dihydro]lauronolic acid, $\text{CN}\cdot\text{C}_8\text{H}_{14}\cdot\text{NH}_2$, this being hydrolysed to the acid. If it is admitted that the carboxyl group of amino[dihydro]lauronolic acid occupies the position of the carbonyl group of camphor, the cyano-group of β -camphornitrilic acid also must be in the β -position, and the transformation of β -camphoramie acid into β -camphornitrilic acid is therefore normal, and is not attended by molecular rearrangement; the constitution of the last-named substance will be represented by one of the formulæ, $\text{CMe}_2\begin{smallmatrix} \text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2 \\ \text{CHMe}-\text{CH}\cdot\text{CN} \end{smallmatrix}$ (Tiemann), and $\text{CMe}_2\begin{smallmatrix} \text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2 \\ \text{CMe}(\text{CN})-\text{CH}_2 \end{smallmatrix}$ (Bredt).

The *amide* of β -camphornitrilic acid, $(\alpha)\text{CN}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NH}_2(\beta)$, crystallises from water or alcohol in white prisms, and melts at $194-196^\circ$. When treated with bromine and sodium hydroxide, it yields the compound, $\text{C}_{19}\text{H}_{32}\text{ON}_4$, melting at 293° , and the *acid*, $\text{C}_{10}\text{H}_{18}\text{O}_3\text{N}_2$, which melts and decomposes at 173° , dissolves readily in dilute mineral acids, yields *isolauronic* acid under the influence of concentrated acids, and is resolved on dry distillation into carbon dioxide, ammonia, and the anhydride of aminodihydrocampholytic acid, $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CO} \\ \text{N} \end{smallmatrix}$, which melts at 189° . The

nitrile of amino[dihydro]lauronolic acid is another product of oxidising the *amide* of β -camphornitrilic acid with alkali hypobromite; the *hydro-*

chloride and *picrate* melt at 290° and 232° respectively, and hydrolysis in sealed tubes at 200° converts it into amino[dihydro]lauronic acid. The *base*, $C_{17}H_{27}N_3$, is produced along with the nitrile of amino[dihydro]lauronic acid; it crystallises from petroleum, melts at 132—133°, and forms a sparingly soluble aurichloride and platinichloride.

The *amide* of α -camphornitrilic acid melts at 130—131°, and yields with alkali the *base*, $C_{10}H_{16}ON_2$, which melts at 280°. The *acid*, $C_{10}H_{16}O_3N_2$, obtained by the action of alkaline hypobromite, crystallises from ethyl acetate in long needles containing $\frac{1}{2}H_2O$; it melts first at 105°, liberating water, then solidifies, and finally decomposes and fuses at 199—200°, yielding the anhydride of amino[dihydro]lauronic acid,

$C_8H_{14}\begin{matrix} NH \\ \diagup \\ CO \end{matrix}$, which melts at 201°.

M. O. F.

Action of Alkaline Sulphides on Potassium Ferrocyanide. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1900, 21, [vii], 204).—No thermal change is observed on mixing dilute solutions of potassium ferrocyanide and sodium sulphide, but nevertheless a slow chemical reaction takes place, resulting in the formation of ferrous sulphide. The ferrocyanide in dilute solutions is slightly dissociated into simple cyanides, and the ferrous cyanide which results, interacts with sodium sulphide yielding ferrous sulphide and sodium cyanide; the presence of the latter cyanide, however, diminishes the dissociation of the double cyanide, and hence a state of equilibrium is soon attained and the amount of sulphide precipitated is very small. G. T. M.

Arsenical Gas from Wall-paper. By PIETRO BIGINELLI (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 210—214 and 242—249).—On growing pure cultures of the arsenic mould, *Penicillium brevicaulis*, obtained by Gosio (*Riv. d'ig. e san. pubbl.*, 1892, 223) in presence of sodium arsenite, energetic decomposition takes place with evolution of gas which, when passed into a hydrochloric acid solution of mercuric chloride, causes the separation of colourless, tabular, triclinic crystals of the double compound $AsHEt_2 + 2HgCl_2$, or $AsHEt_2 : AsHEt_2 + 4HgCl_2$, [$a : b : c = 1.54787 : 1 : 2.37709$; $\alpha = 126^\circ 8' 30''$; $\beta = 123^\circ 14'$; $\gamma = 85^\circ 41' 30''$]. When heated, it begins to soften at 239—240° and decomposes at 255—256°. It can be sublimed in a current of dry air at 100—110°, whilst, on standing in the air, it evolves an odour of garlic, and becomes slightly darkened. When treated with boiling water it dissolves, and on cooling the liquid, it deposits (1) a small quantity of a compound separating in minute prismatic crystals and melting and decomposing at 250—251°. (2) a double compound of tetraethyldiarsonium with

mercuric chloride, $O\begin{matrix} \diagup \\ AsHEt_2 \\ \diagdown \\ AsHEt_2 \end{matrix} + 4HgCl_2$, crystallising in shining scales

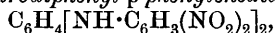
which, when heated in a sealed tube, undergo contraction and incipient fusion at about 270°, but do not melt or completely decompose even at 290°. When the latter compound is treated, in presence of a small quantity of water and an excess of ether, with solid alkali hydroxide, and afterwards with an ethereal solution of iodine, tetraethyldiarsonium iodide, $O(AsHEt_2I)_2$, is obtained in slender, straw-coloured, hygroscopic needles melting at 102°, and this, with silver sulphate, yields the corre-

sponding *sulphate*, $C_8H_{22}OAs_2(SO_4)$, melting at 210° . With silver oxide, the iodide yields *tetraethyl diarsonium oxide*(?), $AsHEt_2 \begin{array}{c} \diagup \quad \diagdown \\ O \end{array} AsHEt_2$, in the form of tufts of deliquescent needles, whilst with nitric acid and potassium permanganate it gives a double compound of tetraethyldiacetydic acid and potassium nitrate, $O(AsHEt_2 \cdot OH)_2 \cdot KNO_3$, separating from alcohol in hygroscopic, acicular, prismatic crystals which melt at $129-131^\circ$ and explode at higher temperatures.

If the gas evolved by the *Penicillium brevicaulis* is passed into mercuric nitrate solution an infusible, insoluble, yellow, amorphous powder of the composition $AsHEt_2 \cdot 2HgNO_3$ is deposited.

It is concluded that the gas developed by wall-paper containing arsenic, and to which poisoning is due, is diethylarsine. T. H. P.

Action of Concentrated Nitric Acid on Bromobenzene. By ERNST BANDROWSKI (*Chem. Centr.*, 1900, ii, 848; from *Bull. Acad. Sci. Cracow*, 1900, 193—198).—By the action of nitric acid of sp. gr. 1.5 on bromobenzene, 1:2:4-bromodinitrobenzene is always formed, together with *o*- and *p*-bromonitrobenzene (compare Parry, *Abstr.*, 1896, i, 352). By the action of *p*-phenylenediamine on the crude product, a red, crystalline substance is obtained, whereas pure bromonitrobenzene does not react with phenylenediamine. When this red substance is boiled with dilute hydrochloric acid, Nietzki and Ernst's dinitrophenylaminodiphenylamine (*Abstr.*, 1890, i, 1114) goes into solution, whilst *tetranitrodiphenyl-p-phenylenediamine*,



remains undissolved. Both these compounds have been found to be formed by the action of phenylenediamine on pure 1:2:4-bromodinitrobenzene. The tetranitro-derivative separates from nitrobenzene in dark red crystals, has a high melting point, and is insoluble in most solvents and in acids. *o*-Bromonitrobenzene is isolated either by distilling in steam or by removing the bromodinitrobenzene in the form of the insoluble dinitrophenylbenzidine by heating the crude product with benzidine and alcohol on the water-bath; under these conditions, *o*-bromonitrobenzene does not act on benzidine, hence Schöpf's *o*-bromonitrobenzene (*Abstr.*, 1889, i, 772) must have been impure, and his product was doubtless dinitrophenylbenzidine.

E. W. W.

***m*-Nitrobenzyl Derivatives.** By ATTILIO PURGOTTI and C. MONTI (*Gazzetta*, 1900, 30, ii, 246—260).—*m*-Nitrobenzyl- ω sulphonic acid, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot SO_3H$, obtained as its sodium salt by the action of sodium sulphite on *m*-nitrobenzyl chloride, separates from water with $1H_2O$ in the form of minute, white crystals melting at 74° ; it is very soluble in alcohol and decomposes alkali carbonates. The sodium (with H_2O), barium (with $3H_2O$), lead, and silver salts were prepared; the methyl ester forms small crystals melting at 77° , and soluble in ether or alcohol.

m-Nitrobenzyl- ω -sulphonic chloride separates from benzene in colourless, rhombic crystals [$a:b:c = 1.86569:1:0.90405$] with a vitreous lustre melting at 100° .

m-Nitrobenzyl- ω -sulphonamide, crystallises from water in thin, spark-

ling laminæ which melt and decompose at 159° , and are moderately soluble in alcohol, more so in hot water.

m-Aminobenzyl-*o*-sulphonic acid, obtained by reducing the nitro-acid in alcoholic solution with ammonium sulphide, separates on the addition of alcohol to its aqueous solution as a white, crystalline precipitate which does not melt, but decomposes at a high temperature.

m-Nitrobenzylaniline, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NHPh}$, prepared by the action of aniline on *m*-nitrobenzyl chloride in alcoholic solution, crystallises from alcohol in slender, orange-red, sparkling needles which melt at 84.5° and are moderately soluble in ether, and more so in alcohol, benzene, chloroform, or carbon disulphide. With acids, it forms readily dissociable salts, its *hydrochloride* forming white leaves or scales which are decomposed by water. *Acetyl-m-nitrobenzylaniline*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPhAc}$, crystallises from ether in long, yellow needles melting at 48° and soluble in chloroform, alcohol, or benzene.

m-Aminobenzylaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NHPh}$, forms long, slender needles which melt at 60° , and are soluble in all the ordinary solvents; its *hydrochloride* melts at 161° .

m-Nitrobenzyl-*o*-toluidine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, prepared similarly to the aniline derivative, crystallises from alcohol in sparkling, orange-yellow scales melting at 62° , and dissolves in benzene, chloroform, carbon disulphide, or ether; the *hydrochloride* separates from hydrochloric acid solutions in white, sparkling leaflets which begin to decompose at 100° and are also decomposed by water, even in the cold.

m-Nitrobenzyl-*m*-toluidine, crystallises from alcohol in microscopic tufts of elongated laminæ which melt at 67° and are soluble in benzene, chloroform, carbon disulphide, or ether, whilst its *hydrochloride* separates from hydrochloric acid in shining white needles which are decomposed by cold water or by heating above 100° .

m-Dinitrodibenzyl-*p*-toluidine, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, crystallises from alcohol in slender, lustrous, yellow needles melting at 86° and is soluble in benzene, chloroform, or carbon disulphide, and to a less extent in ether.

T. H. P.

Iodination of Alkylbenzenes. By ALBERT EDINGER and PAUL GOLDBERG (*Ber.*, 1900, **33**, 2875—2883).—Alkylbenzenes readily give a good yield of moniodo-derivatives when warmed for several hours at 100° with light petroleum, powdered sulphur iodide, and an excess of dilute nitric acid of sp. gr. 1.34; in all cases, the iodine enters the nucleus exclusively. With benzene, 50 per cent. of the calculated quantity of iodobenzene is obtained, and with toluene 60—70 per cent. of a mixture of *o*- and *p*-iodotoluenes. *m*-Xylene yields 75 per cent. of *p*-iodo *m*-xylene, which boils at 220° (Hammerich, *Abstr.*, 1890, 1106, gives 231°) and gives iodotoluic acid [$\text{Me} : \text{CO}_2\text{H} : \text{I} = 1 : 3 : 6$] when oxidised with a mixture of potassium permanganate and dilute nitric acid; the corresponding iodoisophthalic acid could not be obtained, since, on using more concentrated nitric acid in the oxidation, a *diiodo-isophthalic* acid is formed, which crystallises from dilute acetic acid, melts and decomposes at 190° and yields a *copper* salt with $2\text{H}_2\text{O}$. *p*-Iodo *o*-xylene boils at 225° , and on oxidation with a mixture of potass-

ium permanganate and dilute nitric acid, yields a *diiodophthalic acid*, melting and decomposing at 195° ; with dilute nitric acid alone, a mixture of this acid with 4-iodophthalic acid is obtained. *Iodo-p-xylene* boiling at 217° , iodomesitylene (Töhl, Abstr., 1892, 967), and iododurene were obtained from the corresponding hydrocarbons in yields of from 70—80 per cent. of the theoretical; *iodopentamethylbenzene* crystallises from alcohol in white, lustrous plates and melts at 127° , whilst *iodocymene* boils at 80° under 5 mm. pressure. In the case of cymene, the yield of iodo-derivative is only 30—35 per cent. of that calculated, owing to oxidation occurring, whilst from naphthalene a mixture of α - and β -iodonaphthalenes (the latter in very small amount) with nitronaphthalene is obtained, which can only be purified with difficulty.

W. A. D.

Bromination of Alkylbenzenes. By ALBERT EDINGER and PAUL GOLDBERG (*Ber.*, 1900, 33, 2883—2885).—Although sulphur chloride cannot be profitably used to chlorinate alkylbenzenes, sulphur bromide gives good results in brominating; the method adopted is the same as in iodination (preceding abstract), with the exception that the mixture is well cooled during the action. Benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, pentamethylbenzene, and naphthalene give rise only to monobromo-derivatives, but durene yields dibromodurene.

W. A. D.

Application of the Reducing Action of Hyposulphurous Acid. By PAUL GOLDBERGER (*Chem. Centr.*, 1900, ii, 1014; from *Oesterr. Chem.-Zeit.*, 3, 470).—Nitro-compounds containing acid or basic groups are easily reduced by adding zinc dust to a solution of sodium hydrogen sulphite containing the nitro-compound. Neutral compounds such as nitrobenzene or dinitrobenzene are not reduced by this means, but from *p*-nitrophenol, 80 per cent. of the calculated yield of *p*-aminophenol may be obtained; similarly, nitroaniline gives 77 of *p*-phenylenediamine and nitrobenzoic acid 90 per cent. of the calculated yield of anthranilic acid.

E. W. W.

Substituted Nitrogen Chlorides and Bromides derived from *o*-, *m*-, and *p*-Nitroacetanilide. By FREDERICK D. CHATTAWAY, KENNEDY J. P. ORTON, and ROBERT C. T. EVANS (*Ber.*, 1900, 33, 3057—3062. Compare *Trans.*, 1898, 73, 1047; 1899, 75, 134, 789, 797, 800; *Abstr.*, 1900, i, 152).—The presence of a nitro-group in acyl chloro- and bromo-amino-derivatives renders more difficult their change into the corresponding chloro- and bromo-substitution products. Derivatives of *m*- and *p*-nitroacetanilide change very slowly in acetic acid solution, a considerable amount of hydrolysis taking place at the same time, whilst derivatives of *o*-nitroacetanilide do not undergo the change in these circumstances, but yield the corresponding substituted anilines when they are heated under slightly acidified water.

Acetylchloroamino-o-nitrobenzene, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NClAc}$, is prepared by the action of bleaching powder on *o*-nitroacetanilide in acetic acid solution, and crystallises in short prisms melting at 80° . It does not undergo change in acetic acid solution, but when heated with water containing a few drops of acid it yields *o*-nitro-*p*-chloroaniline, melting at 116° .

Acetylbromoamino o-nitrobenzene crystallises in yellow prisms melting at 141° , and when heated with acidified water yields *o*-nitro-*p*-bromoaniline. *Acetylchloroamino-m-nitrobenzene* crystallises in faintly yellow prisms melting at 102° . When its solution in acetic acid is left for some time, *m*-nitroacetanilide and a mixture of *m*-nitro-*p*-chloroacetanilide, and 3-nitro-6-chloroacetanilide is formed, the *m*-nitro-*p*-chloro-compound being produced in the larger proportion. *Acetylbromoamino-m-nitrobenzene* forms lustrous, yellow prisms melting at 135 — 136° , and readily undergoes intramolecular change in acetic acid solution. The resulting anilides yield on hydrolysis *m*-nitro-*p*-bromoaniline as chief product. *Acetylchloroamino-p-nitrobenzene* crystallises in yellow prisms melting at 110 — 111° , and in acetic acid solution yields *p*-nitroacetanilide and *o*-chloro-*p*-nitroacetanilide, melting at 143° . When the nitrogen chloride is heated with sodium carbonate solution, *p*-nitroacetanilide and a small amount of 4:4'-dinitroazobenzene are formed. *Acetylchloroamino-o-chloro-p-nitrobenzene*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NClAc}$, forms light yellow prisms melting at 106° , and does not undergo intramolecular change under any conditions hitherto obtained. *Acetylchloroamino-2:6-dichloro-4-nitrobenzene* crystallises in pale yellow four-sided prisms, melting at 103° . *Acetylbromoamino-p-nitrobenzene* melts at 148° , and in acetic acid solution yields *p*-nitroacetanilide and *o*-bromo-*p*-nitroacetanilide, melting at 129° . *Acetylbromoamino-o-bromo-p-nitrobenzene* crystallises in light yellow twinned prisms which melt and decompose at 151° . As in the case of the corresponding chloro-derivative, it has not been found possible to bring about the intramolecular change of this compound. The 2:6-dibromo-compound melts and decomposes at 156° .

o-Chloro-*p*-nitroacetanilide is only formed in small quantity by the nitration of *o*-chloroacetanilide with a mixture of nitric and sulphuric acids, but is readily obtained by the use of fuming nitric acid at 0° . *p*-Chloro-*o*-nitroacetanilide crystallises in lustrous, yellow needles melting at 104° . *p*-Chloro-*m*-nitroacetanilide crystallises in long needles melting at 145° .
A. H.

Molecular Rearrangement of Disubstituted Thioncarbamic Esters; Phenyliminothiocarbonic Acid Derivatives and Thiosemicarbazidic Esters. By HENRY L. WHEELER and GUY K. DUSTIN (*Amer. Chem. J.*, 1900, **24**, 424—444).—*Methyl methylthioncarbanilate*, $\text{NPhMe} \cdot \text{CS} \cdot \text{OMe}$, prepared by the action of sodium methoxide on methylthioncarbanilic chloride, is a colourless oil which boils at 151 — 152° under 19 mm. pressure; when an alcoholic solution of this compound is boiled with mercuric oxide, *methyl methylcarbanilate*, $\text{NPhMe} \cdot \text{CO}_2\text{Me}$, is obtained as an oil which distils at 117 — 119° under 16 mm. pressure. *Ethyl methylthioncarbanilate*, $\text{NPhMe} \cdot \text{CS} \cdot \text{OEt}$, is a colourless oil which boils at 145 — 150° under 18 mm. pressure and is not affected by boiling hydrochloric acid. *Methyl ethylthioncarbanilate*, $\text{NPhEt} \cdot \text{CS} \cdot \text{OMe}$, boils at 148 — 149° under 18 mm. pressure, crystallises from light petroleum in five-sided plates, and melts at 41 — 42° . Methyl methylthiolcarbanilate may be prepared by heating the corresponding thion ester with methyl iodide for four hours at 103 — 106° ; it boils at 140 — 142° under 16 mm. pressure, crystallises from alcohol in

colourless plates, and melts at 46° , not at 54° as stated by Bertram (Abstr., 1892, 466). *Ethyl methylthiolcarbanilate*, $\text{NPhMe}\cdot\text{CO}\cdot\text{SEt}$, obtained by the action of ethyl iodide on the thion ester at 100° , boils at $160\text{--}163^{\circ}$ under 19 mm. pressure, and melts at $12\text{--}13^{\circ}$. *Methyl ethylthiolcarbanilate*, $\text{NPhEt}\cdot\text{CO}\cdot\text{SMe}$, boils at $148\text{--}149^{\circ}$ under 17 mm. pressure.

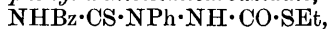
When ethyl dithiocarbonate was left in contact with alcoholic dimethylamine for two weeks, the product was an oil boiling at $205\text{--}206^{\circ}$; estimation of the nitrogen indicated the presence of ethyl dimethylthioncarbamate. By the action of diamylamine on ethyl dithiocarbonate, mercaptan is evolved, but no other definite product could be isolated.

Dimethyl phenyliminothiolcarbonate, $\text{NPh}\cdot\text{C}(\text{SMe})\cdot\text{OMe}$, obtained by the action of sodium methoxide and methyl iodide on methyl thioncarbanilate, is a yellow oil which boils at 133° under 17 mm. pressure, has a peculiar smell, and is converted by hydrogen chloride into methyl thiolcarbanilate; aniline reacts with this substance at $180\text{--}190^{\circ}$, carb-anilide being produced, whilst methylisocarbanilide is apparently not formed; diisobutylamine has very little action on it at $145\text{--}150^{\circ}$. This behaviour of methyl phenyliminothiolcarbonate with bases is in striking contrast with that of the derivatives of benzoyliminothiocarbonic acid, which react readily at a much lower temperature (Wheeler and Johnson, Abstr., 1900, i, 632). *Methyl benzoylthiolcarbanilate*, $\text{NPhBz}\cdot\text{CO}\cdot\text{SMe}$, formed by heating methyl phenyliminothiolcarbonate with benzoyl chloride at 150° , crystallises in needles or prisms, and melts at about 93° . When methyl phenyliminothiolcarbonate is mixed with acetyl chloride, no action takes place, whilst ethyl phenyliminoformate reacts violently with acetyl chloride (Wheeler and Walden, Abstr., 1897, i, 280). *Methyl acetylthioncarbanilate*, $\text{NPhAc}\cdot\text{CS}\cdot\text{OMe}$, prepared by the action of acetyl chloride on the silver salt of methyl thioncarbanilate, crystallises from dilute alcohol, melts at $47\text{--}49^{\circ}$, and when warmed with aniline yields methyl thioncarbanilate and acetanilide. Ethyl phenyliminothiolcarbonate boils at $157\text{--}160^{\circ}$ under 21 mm. pressure, and is converted by hydrogen chloride into ethyl thiolcarbanilate. *Phenyliminothiolisoamylethylcarbonate*, $\text{NPh}\cdot\text{C}(\text{SC}_5\text{H}_{11})\cdot\text{OEt}$, obtained by the action of amyl bromide on the sodium salt of ethyl thioncarbanilate, decomposes on distillation under reduced pressure, and when heated with hydrogen chloride furnishes isoamyl thiolcarbanilate.

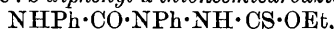
When ethyl phenylthioncarbazinate is warmed with acetyl thiocyanate, hydrogen sulphide is evolved, and a product is obtained which crystallises from alcohol in needles and melts at $93\text{--}94^{\circ}$; this compound is probably 4-acetyl-3-ethoxy-1-phenyl-5-thiotriazolone. Ethyl phenylthioncarbazinate reacts similarly with benzoyl thiocyanate to form a compound, which melts at $136\text{--}138^{\circ}$, and appears to be 4-benzoyl-3-ethoxy-1-phenyl-5-thiotriazolone. The last-mentioned substance is not changed when boiled with hydrochloric acid, ammonia, potassium hydroxide, aniline, or benzoyl chloride, but if heated with alcoholic silver nitrate, the sulphur is eliminated. *Ethyl c-acetylthio-b-phenyl-a-thiolsemicarbazidate*, $\text{NHAc}\cdot\text{CS}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{SEt}$, obtained by the action of ethyl phenylthiolcarbazinate on acetyl thiocyanate, crys-

tallises in prisms, melts at 145° , and is slightly soluble in benzene.

Ethyl c-benzoylthio-b-phenyl-a-thiolsemicarbazidate,

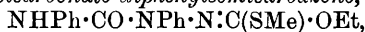


crystallises from benzene in colourless needles or prisms, and melts at $148-150^{\circ}$. *Ethyl c:b-diphenyl-a-thionsemicarbazidate*,



formed when ethyl phenylthioncarbazinate is warmed with phenyl carbimide, crystallises from alcohol in colourless prisms, melts at $114-115^{\circ}$, and, if heated with aniline, yields carbanilide. *Ethyl c:b-diphenyl-a-thiolsemicarbazidate*, $\text{NHPH} \cdot \text{CO} \cdot \text{NPh} \cdot \text{NH} \cdot \text{CO} \cdot \text{SEt}$, obtained by the action of phenylcarbimide on the thiolcarbazinic ester, crystallises in plates, melts at 156° , and is very slightly soluble in alcohol. The corresponding *methyl* ester crystallises from alcohol in small plates, and melts and decomposes at 186° ; it dissolves in sulphuric acid and is reprecipitated on the addition of water, and is not affected by boiling acetic anhydride; when its solution in alkali is boiled, a compound melting at 161° separates in needles. The *benzyl* ester crystallises in prisms or plates, melts at about 150° , and dissolves readily in benzene or hot alcohol, and sparingly in cold alcohol.

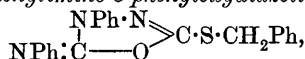
Methyl ethyl thiolcarbonate diphenylsemicarbazone,



obtained by the action of sodium methoxide and methyl iodide on ethyl diphenylthionsemicarbazidate, crystallises from alcohol, melts at $108-109^{\circ}$, and is converted by hydrogen chloride into methyl diphenylthiolsemicarbazidate. *Diethyl thiolcarbonate diphenylsemicarbazone*, $\text{NHPH} \cdot \text{CO} \cdot \text{NPh} \cdot \text{N} : \text{C}(\text{SEt}) \cdot \text{OEt}$, crystallises from dilute alcohol in needles, melts at 111° , dissolves readily in alcohol or benzene, but only sparingly in light petroleum, and when treated with hydrogen chloride yields ethyl thiolsemicarbazidate. *5-Ethoxy-2-*

phenylimino-3-phenyloxidiazoline,
$$\begin{array}{c} \text{NPh} \cdot \text{N} \\ | \quad \diagup \\ \text{NPh} : \text{C} \text{---} \text{O} \end{array} \text{C} \cdot \text{OEt},$$
 obtained by the

action of sodium ethoxide on ethyl *c:b*-diphenyl-a-thionsemicarbazidate, crystallises from alcohol in slender prisms, and melts at 86° . *5-Benzylmercapto-2-phenylimino-3-phenyloxidiazoline*,



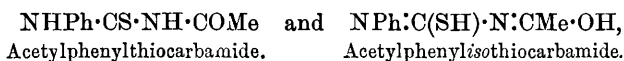
prepared by the action of benzyl chloride on a solution of ethyl diphenylthionsemicarbazidate in aqueous alkali, crystallises from alcohol in colourless needles, melts at $110-112^{\circ}$, and when heated with phosphorus pentachloride is decomposed.

When Bender's salt, $\text{OEt} \cdot \text{CO} \cdot \text{SK}$, is treated with ethyl chlorocarbonate, carbon dioxide, carbon oxychloride, ethyl carbonate and ethyl thiolcarbonate are produced. Ethyl chlorocarbonate reacts with potassium xanthate with formation of carbon dioxide, carbon disulphide, ethyl carbonate, ethyl thioncarbonate, ethyl dithiocarbonate, and the compound, $\text{S}(\text{CS} \cdot \text{OEt})_2$, described by Welde (Abstr., 1877, 314). By the action of ethyl chlorocarbonate on ammonium dithiocarbanilate, carbon oxysulphide, carbanilide, and phenylthiocarbamide are obtained. The phenylhydrazine salt of dithiophenylcarbazinic acid reacts with ethyl chlorocarbonate in benzene solution with formation of ethyl phenylcarbazinate.

E. G.

Reaction of the Isomeric Acetylthiocarbamides with aqueous Sodium Hydroxide. By A. HUGERSHOFF and W. CHR. KÖNIG (*Ber.*, 1900, 33, 3033—3035).—It has already been shown (*Abstr.*, 1900, i, 156) that acetyl-phenylcarbamide and *-isophenyl-*carbamide are decomposed in different ways when heated with 33 per cent. aqueous sodium hydroxide on the water-bath. The first yields a thiocyanate and acetanilide, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{COMe} \rightarrow \text{CN}\cdot\text{SH} + \text{NHPh}\cdot\text{COMe}$, whilst the *iso*-compound yields phenylthiocarbamide and acetic acid, $\text{NPh}\cdot\text{C}(\text{SH})\cdot\text{N}\cdot\text{CMe}\cdot\text{OH} + \text{H}_2\text{O} \rightarrow \text{NHPh}\cdot\text{CS}\cdot\text{NH}_2 + \text{CMeO}\cdot\text{OH}$. The acetyl- α -naphthyl (following abstract) and acetyl- α -tolyl compounds behave in the same way. In the case of the acetyl- β -naphthyl- and acetyl-*p*-tolyl-thiocarbamides, however, the same products (thiocarbamides) are obtained as from the *isothiocarbamides*; presumably the thiocarbamides were first transformed into the *iso*-compounds by the alkali. C. F. B.

Some Isomeric Acetylthiocarbamides of the Naphthalene Series. By A. HUGERSHOFF and W. CHR. KÖNIG (*Ber.*, 1900, 33, 3029—3032).—Isomerism of the kind described in the case of thiocarbamides and *isothiocarbamides* (*Abstr.*, 1900, i, 155) had already been discovered by Freund and Hempel (*Abstr.*, 1895, i, 193) in the case of tetrazole derivatives. In the transformation of the acetylthiocarbamides, it appears that a second hydrogen atom also changes its position, as is represented by the formulæ,



Some naphthyl derivatives have been prepared by the methods already described; these compounds, with their melting points, are: *Acetyl- α -naphthylthiocarbamide*, 146°; *-isothiocarbamide*, 197°, already obtained by Miquel (*Bull. Soc. Chim.*, 1877, [ii], 28, 103); *acetyl- β -naphthyl-thiocarbamide*, 145°; *isothiocarbamide*, 158°. C. F. B.

Preparation of Pentachlorophenol. By ÉTIENNE BARRAL and L. JAMBON (*Bull. Soc. Chim.*, 1900, [iii], 23, 822—825).—Of the various methods which have been devised for the preparation of pentachlorophenol, the three most practical and economical are those in which phenol is chlorinated in the presence of antimony chloride (4—5 per cent.), iodine (2—3 per cent.), or anhydrous ferric chloride (3—4 per cent.), the last named reagent being, perhaps, the most efficient. The use of larger quantities than those stated causes the formation of resinous matters and of perchlorodioxydiphenylene, whilst if smaller quantities are employed the time required is increased although a purer product is obtained. It is important that the chlorine employed should be perfectly dry, in order to avoid the formation of tetrachloroquinone, that the temperature should not rise above 135—140°, and that the chlorinating agent should be added, not at the commencement of the operation, but only when the increase in weight observed corresponds with the conversion of the phenol into trichlorophenol. The crude product is washed with light petroleum, dissolved in sodium hydroxide, and 2—3 per cent. of sodium peroxide

added; the pentachlorophenol is finally precipitated by adding a slight excess of hydrochloric acid, and crystallised from hot benzene.

N. L.

Some Pentachlorophenoxides. By L. JAMBON (*Bull. Soc. Chim.*, 1900, [iii], 23, 825—829).—The metallic pentachlorophenoxides may be obtained either by the direct action of pentachlorophenol on the metallic hydroxide or, in the case of the more insoluble compounds, by double decomposition. They are solid substances, generally crystallising in long needles or flattened prisms belonging to the orthorhombic system. The lead, silver, copper, and mercury compounds are insoluble in water, whilst the lithium and calcium derivatives are very soluble; all are insoluble in benzene or light petroleum. The pentachlorophenoxides are decomposed by acids, even by carbon dioxide, and when heated they yield a metallic chloride and perchlorodioxidyphenylene. The following compounds are described in the paper: $\text{C}_6\text{Cl}_5\text{OLi}, \text{H}_2\text{O}$; $\text{C}_6\text{Cl}_5\text{ONa}, \text{H}_2\text{O}$; $\text{C}_6\text{Cl}_5\text{OK}, \text{H}_2\text{O}$; $\text{C}_6\text{Cl}_5\text{ONH}_4, 2\text{H}_2\text{O}$; $(\text{C}_6\text{Cl}_5\text{O})_2\text{Ca}$; $(\text{C}_6\text{Cl}_5\text{O})_2\text{Sr}, 2\text{H}_2\text{O}$; $(\text{C}_6\text{Cl}_5\text{O})_2\text{Ba}, 2\text{H}_2\text{O}$; $(\text{C}_6\text{Cl}_5\text{O})_2\text{Mg}, 10\text{H}_2\text{O}$; $(\text{C}_6\text{Cl}_5\text{O})_2\text{Zn}, \text{H}_2\text{O}$; $(\text{C}_6\text{Cl}_5\text{O})_2\text{Co}, 4\text{H}_2\text{O}$; $(\text{C}_6\text{Cl}_5\text{O})_2\text{Ni}, 8\text{H}_2\text{O}$; $(\text{C}_6\text{Cl}_5\text{O})_2\text{Cu}, \frac{1}{2}\text{H}_2\text{O}$; $(\text{C}_6\text{Cl}_5\text{O})_2\text{Hg}, 2\text{H}_2\text{O}$; $(\text{C}_6\text{Cl}_5\text{O})_2\text{Pb}$; $\text{C}_6\text{Cl}_5\text{OAg}$; $\text{OH}\cdot\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{H}_2\text{Ph}$.

N. L.

Millon's Reaction. By WILHELM VAUBEL (*Zeit. angew. Chem.*, 1900, 1125—1130).—The author summarises the results he has obtained as follows: 1. The action of Millon's reagent (mercurous nitrate and nitric oxide) on phenol is represented by the following equations: (a) $2\text{C}_6\text{H}_5\cdot\text{OH} + 2\text{NO} + \text{O} = 2\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{OH} + \text{H}_2\text{O}$; (b) $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{OH} + 4\text{HgNO}_3 + 3\text{NO} + 3\text{C}_6\text{H}_5\cdot\text{OH} = \text{OH}\cdot\text{N}\left(\text{N}\left\langle\begin{smallmatrix} \text{O}\cdot\text{C}_6\text{H}_4 \\ \text{O}-\text{Hg} \end{smallmatrix}\right\rangle\text{O}\right)_4 + 3\text{NO}_2 + 3\text{H}_2\text{O}$. 2. On heating with aqueous sodium hydroxide this substance loses its mercury, and a reddish brown soluble compound is formed which is precipitated by acids, the reaction being apparently as follows: $\text{OH}\cdot\text{N}\left(\text{N}\left\langle\begin{smallmatrix} \text{O}\cdot\text{C}_6\text{H}_4 \\ \text{O}-\text{Hg} \end{smallmatrix}\right\rangle\text{O}\right)_4 + 9\text{NaOH} = \text{ONa}\cdot\text{N}(\text{C}_6\text{H}_4\cdot\text{ONa})_2(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{ONa})_2 + 4\text{Hg} + 5\text{H}_2\text{O} + 2\text{NaNO}_2 + 2\text{NaNO}_3$. 3. The compound thus obtained takes up with 4 atoms of bromine in the phenol groups and probably one also in place of the hydroxyl group, the substance $\text{NBr}(\text{C}_6\text{H}_3\text{Br}\cdot\text{OH})_2(\text{O}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{OH})$ being thus formed. 4. Millon's reaction is not given by di-ortho and di-meta-substituted compounds. 5. Of the naphthols, only the β -compound yields a substance similar to that obtained from phenol. All the other naphthol derivatives investigated yielded nitroso-compounds.

L. DE K.

A General Method for the Preparation of Mixed Phenyl Alkyl Carbonates; Pentachlorophenyl Alkyl Carbonates. By ÉTIENNE BARRAL (*Compt. rend.*, 1900, 131, 679—681).—Many of the methods that might be expected to yield phenyl alkyl carbonates give unsatisfactory results, especially with substituted phenols, but good yields are obtained by the action of carbon oxychloride, dissolved in toluene, on a solution of the phenol in an excess of the alcohol to which an alkali hydroxide has been added in proportion equivalent to

the phenol. In this way, the author has prepared several pentachlorophenyl alkyl carbonates; they are insoluble in water, but dissolve readily in organic solvents and are only slowly attacked by alkalis. *Pentachlorophenyl methyl carbonate* forms colourless needles melting at 137° ; the corresponding *ethyl* ester forms large, colourless prisms melting at 66° ; the *propyl* ester, small, micaceous crystals melting at 57° ; the *isopropyl* ester, mamelons of small crystals which melt at 58° ; the *butyl* ester, very large, colourless prisms melting at 59° ; the *isobutyl* ester, very large, colourless, flattened prisms melting at 58° ; the *isoamyl* ester, small needles melting at 54° ; the *heptyl* ester, an oily liquid decomposed by heat; the *octyl* ester, an oily liquid very easily decomposed by heat; the *allyl* ester, small, white, nacreous, micaceous crystals melting at 57° ; the *benzyl* ester, small, white needles melting at 116° .
C. H. B.

Relation between the Constitution of Quinols and their Tendency to Form Quinones. By FRIEDRICH KEHRMANN (*Ber.*, 1900, 33, 3066—3067).—Kauffmann has stated (*Abstr.*, 1900, i, 480) that the fact that tetrachloroquinol is oxidised by trichloroquinone forms an exception to the author's rule (*Abstr.*, 1898, i, 439). This is not the case, since the tetrachloroquinol has a higher molecular weight than trichloroquinol, and this more than counterbalances the effect of the fourth chlorine atom, which in aromatic compounds does not act as a very strongly negative radicle.
A. H.

Energy of Non-carboxylic Organic Acids. By GIULIO COFFETTI (*Gazzetta*, 1900, 30, ii, 235—246).—The energies of chloroanilic, bromoanilic, nitroanilic, leuconic, croconic, and rhodizonic acids have been determined, the first three by the sugar inversion method, and the others by measuring their electrical conductivities. Taking the energy of hydrochloric acid as 1, the energies of nitroanilic, bromoanilic, and chloroanilic acids have the values 0.684, 0.322, and 0.319 respectively. Croconic acid is a moderately strong acid, rhodizonic acid less so, whilst leuconic acid has very feeble acid properties. The results show that the accumulation of carbonyl groups in a molecule is not sufficient to increase its acidic energy, as much depends on the structural arrangement. The electro-negative energy given to a molecule by a carbonyl group seems to be less than that conferred by the entry of a chlorine or bromine atom or a nitro-group under the same conditions.
T. H. P.

Hydrolysis of Acid Amides. By EMMET REID (*Amer. Chem. J.*, 1900, 24, 397—424. Compare *Abstr.*, 1899, i, 507).—The author has continued his study of the hydrolysis of substituted benzamides, and has obtained results which are in accord with those previously published (*loc. cit.*).

The following values for the constant K have been obtained by means of dilute hydrochloric acid.

o-Phenoxybenzamide, *0.00562 and *0.00568; *o*-dimethylaminobenzamide, 0.00120; *o*-bromobenzamide, 0.00177; *p*-methoxybenzamide, 0.0131; *p*-ethoxybenzamide, 0.0185; *m*-hydroxybenzamide, 0.0114; *m*-iodobenzamide, *0.0189, and *p*-iodobenzamide, *0.0164.

The alkaline hydrolysis was effected by the aid of solution of barium hydroxide. The hydrochloric acid employed to estimate the ammonia produced was standardised in the following manner. A known weight of *p*-nitrobenzamide was treated with excess of solution of sodium hydroxide and distilled into a measured quantity of the acid. The author recommends this method for general use, since *p*-nitrobenzamide can be readily obtained in a pure state, and yields the calculated amount of ammonia when distilled with alkali. The following values for the constant *K* were obtained :

| | | | |
|----------------------------|--------------------------|------------------------|------------------------|
| Benzamide | 0.0943 | | |
| | Ortho. | Meta. | Para. |
| Toluamide | { 0.00508 } 0.00503 } | { 0.0780 } 0.0752 } | { 0.0623 } 0.0596 } |
| Nitrobenzamide | ? | 0.530 | — |
| Chlorobenzamide | { 0.0435 } 0.0489 } | — | *0.180 |
| Hydroxybenzamide | 0.00616 | 0.0180 | — |
| Bromobenzamide | 0.0291 | { *0.282 } 0.273 } | *0.180 |
| Iodobenzamide | 0.0130 | *0.245 | *0.159 |
| Methoxybenzamide | 0.0528 | — | 0.0462 |
| Ethoxybenzamide | 0.0360 | — | — |
| Dimethylaminobenzamide ... | 0.0152 | — | — |
| Phenoxybenzamide | *0.0427 | — | — |
| Aminobenzamide | — | { 0.0877 } 0.0885 } | { 0.0178 } 0.0202 } |

* These results were obtained when the concentration of the amide was half that employed in the other cases.

In the case of *o*-nitrobenzamide, anomalous results were obtained ; in one series, the velocity decreased from 0.0522 (after $\frac{1}{2}$ hour) to 0.0272 (after 4 hours). It was found that when *o*-nitrobenzamide is boiled with baryta water, it yields half the calculated amount of ammonia, and this quantity is not increased by prolonged boiling. The alkaline solution rapidly becomes red on heating, and, if acidified, a red, flaky precipitate is produced which is soluble in alcohol.

E. G.

Oxidation of Hippuric Acid to Carbamide. By ADOLF JOLLES (*Ber.*, 1900, 33, 2834—2837. Compare Abstr., 1900, ii, 450—454).—Glycine is not acted on by permanganate in acid solution, but is readily oxidised by it in alkaline solution. Creatinine, similarly, is not oxidised by the acid reagent, whereas ethyl aminoacetate is immediately oxidised. The author attributes this to the closed ring constitutions of glycine and creatinine, and the open chain constitution of the ester and alkali salts of the former.

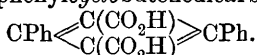
When hippuric acid is boiled with acid permanganate, in other words, when glycine is oxidised at the moment of formation, a theoretical yield of carbamide is obtained.

J. J. S.

Condensation of α -Bromoallocinnamic Acid. By W. MANTHEY (*Ber.*, 1900, 33, 3081—3086).—The author has already shown (*Abstr.*, 1899, i, 894) that the product obtained by the action of sulphuric acid on α -bromoallocinnamic acid has the formula $(C_9H_5OBr)_x$, and not $C_7H_{12}O_2Br_2$, as supposed by Leuckart (*Abstr.*, 1882, 615). On reduction with platinised zinc dust and acetic acid, it yields a mixture of *truxone* and *dihydrotruxone*, $(C_9H_8O)_x$; the latter is identical with Leuckart's reduction product and is converted by oxidising agents into *truxone*.

Estimations of the molecular weight of dihydrotruxone in boiling benzene or acetone show that it has the formula $C_{18}H_{16}O_2$, from which it may also be inferred that *truxone* is $C_{18}H_{18}O_2$, contrary to the view taken by Liebermann; this confirms the opinion expressed by Kipping (*Trans.*, 1894, 65, 975).

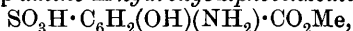
Determinations of the molecular weight of triphenyltrimesic acid and its ethyl esters indicate that this acid also has the bimolecular formula $C_{18}H_{12}O_4$, and the molecular conductivity of its sodium salt is in accordance with this conclusion; $\mu 1024 - \mu 32 = 21.07$, which is approximately the number characteristic of dibasic acids. The acid is therefore, in reality, diphenylcyclobutenedicarboxylic acid,



Chlorotruxone, $C_{18}H_{10}O_2Cl_2$, from α -chloroallocinnamic acid, separates from xylene in white, cubic crystals, is sparingly soluble in the ordinary media, and melts and decomposes at 290° . A. L.

Sulphonic Derivatives of Methyl-*p*-amino-*m*-hydroxybenzoate (Orthoform). By PAUL JACOB (*J. Pharm.*, 1900, [vi], 12, 210—217).—When methyl *p*-amino-*m*-hydroxybenzoate is dissolved in sulphuric acid, a dark green coloration is produced, whereas the corresponding *m*-amino-derivative, on similar treatment, gives a red coloration.

Methyl hydrogen p-amino-m-hydroxysulphobenzoate,



obtained by the action of fuming sulphuric acid, crystallises, with $3H_2O$, in slender needles which melt at 208 — 209° , and is very readily soluble in water or alcohol. The sodium, calcium, barium, zinc, and copper salts of the monomethyl ester were prepared.

H. R. LE S.

Presence of Homologous Coumarones in Coal-tar. By RICHARD STOERMER and JOHANNES BOES (*Ber.*, 1900, 33, 3013—3020).—A fraction of coal-tar boiling at 185 — 195° was shaken with sulphuric acid, poured into water, extracted with ether, and the product separated from volatile hydrocarbons by a current of superheated steam. Subsequent dry distillation gave a neutral oil consisting of hydrindene, methylcoumarones, and substances of higher boiling point, together with a phenolic mixture containing *o*-, *m*-, and *p*-cresols. From these observations, the presence of 6-, 5- or 3-, and 4-methylcoumarones in the tar is deduced.

A fraction boiling at 215 — 225° , when treated in a similar way,

gave a product which was identified as 4 : 6-dimethylcoumarone, whilst the phenolic part of the distillate consisted of *as-m*-xylenol.

T. M. L.

Partial Conversion of 'Phenyl-oxyacrylic Acid' into Phenylpyruvic Acid. By EMIL ERLÉNMEYER, jun. (*Ber.*, 1900, 33, 3001—3002. Compare Abstr., 1891, 1482).—The constitution of phenylethylene-oxide-carboxylic acid (phenyl-oxyacrylic acid),

$\text{CO}_2\text{H} \cdot \text{CH} \begin{array}{c} \text{CHPh} \\ \diagup \text{O} \end{array}$, is confirmed by its partial conversion into phenylpyruvic acid, when heated with hydrochloric acid; this change is analogous to the conversion of phenylethylene oxide into phenylacetaldehyde (Breuer and Zincke, Abstr., 1878, 886). T. M. L.

Esterification of Unsymmetrical Di- and Poly-basic Acids.

III. Esterification of 3- and 4-Nitrophthalic Acid. By RUDOLF WEGSCHEIDER and ALFRED LIPSCHITZ (*Monatsh.*, 1900, 21, 787—812. Compare Abstr., 1900, i, 657, 658).—The *monomethyl* ester of 3-nitrophthalic acid, in which the free carboxyl group occupies the 1-position, that is, the α -compound according to the nomenclature of Wegscheider (*Monatsh.*, 16, 139), crystallises with H_2O , melts, when anhydrous, at 144—145°, has a conductivity $K = 0.2$, and is obtained by any of the following methods:—the partial hydrolysis of the diethyl ester; the action of methyl iodide on the *potassium hydrogen* salt, which crystallises, with $1\frac{1}{2}\text{H}_2\text{O}$, in long, slender, silky needles; the action of methyl alcohol on the anhydride, and the action of methyl alcohol on the free acid in the absence of strong mineral acids. The β -*monomethyl ester* crystallises in pale yellow tablets, melts at 157—158°, has a conductivity $K = 1.5$, and is obtained by the action of methyl alcohol on the acid in the presence of hydrochloric or sulphuric acids, it differs from the α -ester in giving no precipitate with solutions of ferric chloride, lead acetate, or alum.

When 4-nitrophthalic acid is subjected to all the above methods of esterification, only the diethyl ester and one monomethyl ester are obtained; this *monomethyl ester* crystallises with H_2O and melts at 129°. *Potassium hydrogen 4-nitrophthalate* crystallises with H_2O .

R. H. P.

Derivatives of *o*-Xylylidene-phthalide. By PAUL GOLDBERG (*Ber.*, 1899, 33, 2818—2824).—*o*-Xylylidene-phthalide dinitrite, $\text{C}_7\text{H}_7 \cdot \text{CH}(\text{NO}_2) \cdot \text{C}(\text{NO}_2) \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \text{O} \end{array} \text{CO}$, obtained by adding liquid nitrogen peroxide to *o*-xylylidene-phthalide dissolved in cooled benzene or acetic acid, is crystalline and melts and decomposes at 158—159°.

Nitro-o-xylylidene-phthalide, $\text{C}_7\text{H}_7 \cdot \text{C}(\text{NO}_2) \cdot \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \text{O} \end{array} \text{CO}$, produced by warming the foregoing compound with moist amyl alcohol, forms beautiful, lemon-yellow crystals melting at 167—169°. The *sodium* derivative, $\text{C}_{16}\text{H}_{11}\text{O}_5\text{NNa}_2 \cdot 2\text{H}_2\text{O}$, forms white crystals which become yellow at 80°.

On dissolving nitroxylylidene-phthalide in sodium hydroxide and saturating the solution with oxalic acid, phthalic anhydride crystal-

lises out and *o*-tolylnitromethane, $C_6H_4Me \cdot CH_2 \cdot NO_2$, remains in solution, and may be separated by distillation in a current of steam. This substance dissolves in aqueous sodium hydroxide, and on adding acid to the solution, the isonitro-derivative is precipitated as a white, crystalline substance, which slowly reverts to the normal form.

2-*Tolyldiketohydrindene*, $C_6H_4 \langle \begin{smallmatrix} CO \\ CO \end{smallmatrix} \rangle CH \cdot C_7H_7$, formed when *o*-xylylidene-phthalide is boiled with a solution of sodium methoxide, separates from boiling alcohol in beautiful, yellowish crystals melting at 179—180°. The *dioxime*, $C_{16}H_{12}(NOH)_2$, crystallises from alcohol and melts at 212°. The *phenylhydrazone*, $C_{16}H_{12}O \cdot N_2HPh$, forms yellow crystals melting at 173—174°.

2-*Tolyl-2-methyldiketohydrindene*, $C_6H_4 : (CO)_2 : CMe \cdot C_7H_7$, prepared from tolyldiketohydrindene by treatment with sodium methoxide and methyl iodide, is a yellow crystalline substance melting at 149°. The corresponding *ethyl*, *benzyl*, and *benzoyl* derivatives melt at 179°, 179°, and 181° respectively.

Bromo-2-o-tolyldiketohydrindene, $C_{16}H_{11}O_2Br$, separates from alcohol in yellow crystals and melts at 171—172°. *Dichloro-2-o-tolyldiketohydrindene*, $C_{16}H_{10}O_2Cl_2$ melts at 125·5°.

Nitro-o-tolyldiketohydrindene, $C_{16}H_{11}O_2 \cdot NO_2$, obtained by the action of nitrogen peroxide on *o*-tolyl diketohydrindene, forms white crystals melting at 131°. By using fuming nitric acid, a *dinitro*-derivative $C_{16}H_{10}O_2(NO_2)_2$ melting at 159—160° is obtained.

o-*Cyano-o-xylylidene-phthalide*, $C_7H_7 \cdot C(CN) : C \langle \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} \rangle CO$, formed when *o*-tolylacetonitrile and phthalic anhydride are heated at 240—245° with a little anhydrous sodium acetate, melts at 191—192°. *o*-Tolylthioacetamide, $C_7H_7 \cdot CH_2 \cdot CS \cdot NH_2$, melts at 115°, and when heated with ethylene dibromide, is converted into *o-xylylthiazoline*, $C_8H_9 \langle \begin{smallmatrix} S \cdot CH_2 \\ N \cdot CH_2 \end{smallmatrix} \rangle$. The latter is oily, but yields a sparingly soluble *picrate*, $C_{11}H_{13}NS, C_6H_5O_7N_3$, melting at 154—155°, and a *platinichloride*, $(C_{11}H_{13}NS)_2, H_2PtCl_6$, which forms beautiful, yellow crystals melting at 191°.

5-*Methyl-2-o-xylylthiazoline*, $C_7H_7 \cdot CH_2 \cdot C \langle \begin{smallmatrix} S \cdot CHMe \\ N \cdot CH_2 \end{smallmatrix} \rangle$, prepared from *o*-tolylthioacetamide and β -bromopropylamine, is a yellow oil with an odour resembling that of coniine, and gives a sparingly soluble *picrate*, $C_{13}H_{15}NS, C_6H_5O_7N_3$, melting at 126° and a *platinichloride*, $(C_{12}H_{15}NS)_2, H_2PtCl_6$, melting at 156—157°. A. L.

Explanation of Tautomeric Phenomena. By PAUL RABE (*Annalen*, 1900, 313, 129—207. Compare Knorr, *Abstr.*, 1899, i, 673).—The preliminary portion of the paper is devoted to a discussion of earlier memoirs dealing with the subject of tautomerism, and contains a useful summary of existing information relating to this phenomenon. With the object of studying the conditions which influence the stability of the desmotropic forms of a tautomeric substance, the author has investigated the various modifications of ethyl benzylidenebisacetoacetate and of ethyl methylenebisacetoacetate.

No fewer than twenty-two modifications of ethyl benzylidenebisacetoacetate are theoretically possible, this number being composed of five double ketonic esters, $\text{CHPh}(\text{CHAc}\cdot\text{CO}_2\text{Et})_2$, twelve half enolic esters, $\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CHPh}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CMe}\cdot\text{OH}$, and five double enolic esters, $\text{CHPh}[\text{C}(\text{CO}_2\text{Et})\cdot\text{CMe}\cdot\text{OH}]_2$, and of these, three double ketonic esters (β -esters) and three half enolic esters (α -esters) have been characterised.

When ethyl benzylidenebisacetoacetate is prepared by Knoevenagel's method (Abstr., 1895, i, 48), namely, by condensing benzaldehyde with ethyl acetoacetate (2 mols.) under the influence of piperidine, three different esters are produced; they do not give directly a coloration with ferric chloride, and must be therefore regarded as double ketonic esters. The β_1 -ester is the chief product, being the compound described already by Hantzsch (Abstr., 1886, 77); it crystallises from alcohol in slender needles, and melts at $149\text{--}150^\circ$. The β_2 -ester forms a small proportion of the mixture, and crystallises from alcohol in rhombs melting at 154° . The β_3 -ester occurs in very small quantities, and crystallises from dilute alcohol in prismatic needles which contain $2\text{H}_2\text{O}$ and melt at $90\text{--}93^\circ$; the anhydrous substance melts at $107\text{--}108^\circ$.

On treating the β_1 -ester with sodium ethoxide, even when the latter is in excess, there is produced the sodium derivative of the α_1 -ester, $\text{C}_{19}\text{H}_{23}\text{O}_6\text{Na}$, which crystallises in leaflets containing 1 mol. of alcohol, and melts at $132\text{--}135^\circ$, when it decomposes. When water acts on this salt, the β_1 -ester is regenerated, but sulphuric acid liberates the α_1 -ester, which crystallises in small prisms containing $1\text{H}_2\text{O}$, and melting at $68\text{--}70^\circ$; if maintained at the melting point, it becomes transformed into the β_1 -ester, but when the temperature is rapidly raised, water is removed at 100° , and the fused mass solidifies, afterwards melting at $148\text{--}150^\circ$, the melting point of the β_1 -ester. The α_1 -ester develops an intense reddish-violet coloration with ferric chloride, and is therefore the half-enolic modification; the hydrated substance becomes anhydrous when the solution in absolute ether, is agitated with anhydrous sodium sulphate, and in this condition melts at 60° .

The α_2 -ester, prepared in the same way from the β_2 -ester, is a transparent, viscous oil which gradually solidifies, regenerating the β_2 -ester; the sodium derivative crystallises in orange coloured, hygroscopic leaflets, which evolve gas and melt to a viscous liquid at $90\text{--}100^\circ$. The α_3 -ester melts at $65\text{--}67^\circ$.

The experiments described by Schiff (Abstr., 1899, i, 366) suggest that the β -esters are interconvertible, but the author has found that this is not the case, and that Schiff's putative isomerides melting at $134\text{--}135^\circ$ and 120° are merely mixtures.

Knorr (*loc. cit.*) has studied the conditions of equilibrium obtaining among the isomeric ethyl diacetylsuccinates, and found that it is from the proportion of isomerides in fused mixtures only that conclusions regarding their relative stability can be drawn, the proportion in the case of dissolved mixtures being too dependent on the nature of the solvent. As in the series investigated by Knorr, the stability limits of the ethyl benzylidenebisacetoacetates appear to coincide with their melting points, but in the case of the α_2 -ester this statement cannot be made with certainty. Both in the fused and dissolved states, the

esters yield allelotropic mixtures, consisting in each case of the β -ester associated with the corresponding α -compound. M. O. F.

Bis-*p*-dimethyl-*o*-carboxycinnamic and Bisdimethylphthalic Acids from the Oxidation of Bisdihydrosantinic Acid. By GIUSEPPE GRASSI-CRISTALDI and G. TOMARCHIO (*Gazzetta*, 1900, 30, ii, 122—127).—The oxidation of bisdihydrosantinic acid by means of 4 per cent. permanganate solution yields the following two acids.

*Bis-p-dimethyl-*o*-carboxycinnamic acid*, $C_{22}H_{24}O_8$, gives a *barium* salt which is soluble and a *silver* salt insoluble in water.

Bis-p-dimethylphthalic acid, $C_{20}H_{18}O_8$, which is also obtained by oxidation of the former compound, yields a *barium* salt insoluble in water. T. H. P.

Iodine Derivatives of [Acetophenone]. By A. COLLET (*Bull. Soc. Chim.*, 1900, [iii], 23, 829—832. Compare Abstr., 1899, i, 434).—The following iodine derivatives of acetophenone have been prepared by warming alcoholic solutions of the corresponding chlorine or bromine compounds with potassium iodide at 60—70°.

p-Chlorophenyl iodomethyl ketone, $C_6H_4Cl \cdot CO \cdot CH_2I$, crystallises in colourless, silky needles melting at 75·5°; on oxidation with potassium permanganate in alkaline solution, it yields *p*-chlorobenzoic acid.

p-Bromophenyl iodomethyl ketone, $C_6H_4Br \cdot CO \cdot CH_2I$, crystallises in white needles melting at 90° and yields *p*-bromobenzoic acid when oxidised with alkaline potassium permanganate.

Phenyl diiodomethyl ketone, $COPh \cdot CHI_2$, was obtained as a heavy, brown, oily liquid which boils and decomposes above 200° and yields benzoic acid on oxidation.

p-Chlorophenyl diiodomethyl ketone, $C_6H_4Cl \cdot CO \cdot CHI_2$, forms small, colourless crystals melting at 111—112° and yields *p*-chlorobenzoic acid on oxidation.

p-Bromophenyl diiodomethyl ketone, forms colourless crystals which melt at 119—120° and when oxidised yields *p*-bromobenzoic acid.

Phenyl triiodomethyl ketone, $COPh \cdot CI_3$, is a heavy, brown, oily liquid which decomposes when heated and yields benzoic acid on oxidation.

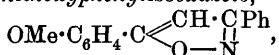
The compounds described above are all insoluble in water, but more or less soluble in the usual organic solvents; they are quickly decomposed on exposure to light, iodine being liberated, and their vapours strongly irritate the eyes. N. L.

Action of Sodium Methoxide on Anisylidene Acetophenone Dibromide. By F. J. POND and ARTHUR S. SHOFFSTALL (*J. Amer. Chem. Soc.*, 1900, 22, 658—685. Compare Abstr., 1900, i, 102, and Wislicenus, *ibid.*, i, 37).—Anisylideneacetophenone dibromide separates from ethyl acetate in large crystals melting at 139—140°, but when boiled for a short time with alcohol yields an additive compound of *bromoanisylideneacetophenone* and *ethyl alcohol*,

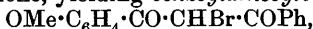
$OMe \cdot C_6H_4 \cdot CHBr \cdot CH(OEt) \cdot COPh$
or $OMe \cdot C_6H_4 \cdot CH(OEt) \cdot CHBr \cdot COPh$; this melts at 73·5—74·5°, and when carefully heated at 155—160° evolves ethyl alcohol and yields *bromoanisylideneacetophenone*, which crystallises from ethyl acetate in large plates melting at 94·5°. The additive compound with methyl

alcohol crystallises in colourless needles melting at 102° , and the compound with propyl alcohol is an oil.

The substance melting at $131-132^{\circ}$, previously described as benzoylanisoylmethane, is now shown to be α -hydroxyanisylideneacetophenone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{COPh}$, the copper derivative, $\text{C}_{32}\text{H}_{26}\text{O}_6\text{Cu}$, forms small, pale green needles melting and decomposing at $247-249^{\circ}$, and when warmed with dilute hydrochloric acid regenerates the pure hydroxyketone. Hydroxylamine hydrochloride reacts with an alcoholic solution of α -hydroxyanisylideneacetophenone, yielding 3-phenyl-5-p-methoxyphenylisooxazole,



which crystallises in pearly flakes melting at 120° , and is insoluble in water or alkalis. An isomeric phenyl-p-methoxyphenylisooxazole obtained when anisylideneacetophenone dibromide is treated with hydroxylamine hydrochloride and an excess of potash, crystallises in slender needles melting at $127-128^{\circ}$, and is soluble in most organic solvents. Bromine reacts with a chloroform solution of α -hydroxyanisylideneacetophenone, yielding benzoylanisoylbromomethane,



which melts at 128° ; it dissolves in most organic solvents, and its alcoholic solution is not coloured by ferric chloride.

In the preparation of α -hydroxyanisylideneacetophenone, a small amount of a compound melting at 90° is always obtained, which probably has the constitution $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{COPh}$.

The first product of the action of sodium ethoxide on anisylideneacetophenone dibromide is a heavy oil, probably α -ethoxyanisylideneacetophenone, which on treatment with dilute acids is hydrolysed to α -hydroxyanisylideneacetophenone.

The same hydroxy-compound is also formed when α -bromoanisylideneacetophenone is treated first with sodium methoxide or ethoxide and then with dilute acids.

J. J. S.

Chemical Action of Light. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1900, 33, 2911-2913).—The product obtained by the action of light on a mixture of alcohol and benzophenone (Oechsner de Coninck and Devrien, *Abstr.*, 1900, i, 502) is Linne-mann's benzopinacone, $\text{OH}\cdot\text{CPh}_2\cdot\text{CPh}_2\cdot\text{OH}$ (*Annalen*, 1865, 133, 26), and the product from alcohol and acetophenone is acetophenonepinacone, $\text{OH}\cdot\text{CMePh}\cdot\text{CMePh}\cdot\text{OH}$.

T. M. L.

Derivatives of Benzophenone. V and VI. By PIETRO BARTOLLOTTI (*Gazzetta*, 1900, 30, ii, 224-229 and 229-234. Compare *Abstr.*, 1899, i, 368).—Benzoyl-m-tolyl benzoate, $\text{C}_6\text{H}_5\text{MeBz}\cdot\text{OBz}$, prepared by heating m-tolyl benzoate with benzoyl chloride in presence of zinc chloride, crystallises from alcohol in silky, white needles melting at $104-105^{\circ}$ and is soluble in the ordinary solvents, but insoluble in sodium hydroxide. On hydrolysis with alcoholic sodium hydroxide, it yields benzoyl-m-cresol.

Benzoyl-m-cresol, $\text{C}_6\text{H}_5\text{MeBz}\cdot\text{OH}$, separates from a mixture of benzene and light petroleum in small, colourless crystals melting at

128°, and is soluble in sodium hydroxide solution, giving a yellow liquid, and also in the ordinary solvents. *Benzoyl-m-tolyl acetate*, $C_6H_3MeBz \cdot OAc$, is an almost colourless liquid soluble in the ordinary solvents, but insoluble in sodium hydroxide solution.

Benzoyl-m-tolyl methyl ether, $C_6H_3MeBz \cdot OMe$, obtained by heating benzoyl *m*-cresol with methyl alcoholic potassium hydroxide and methyl iodide, is a dense, colourless liquid very soluble in the ordinary solvents, but insoluble in sodium hydroxide solution.

Benzoyl-o-tolyl benzoate, prepared similarly to the *m*-compound, separates from alcohol in white, silky crystals melting at 99·5°, and is soluble in the ordinary solvents, but insoluble in sodium hydroxide solution.

Benzoyl-o-cresol, obtained by hydrolysing the previous compound, is deposited from alcohol in white, silky crystals which melt at 172—172·5° and dissolve in the ordinary solvents, and in sodium hydroxide solution. *Benzoyl-o-tolyl acetate* is a dense, pale yellow liquid insoluble in sodium hydroxide, but soluble in the ordinary solvents.

T. H. P.

The Ketones of Anthracene. By EDUARD LIPPMANN and PAUL KEPPICH (*Ber.*, 1900, 33, 3086—3092).—When a solution of benzoyl chloride and anthracene in carbon disulphide is heated with freshly-prepared aluminium chloride, a crystalline, apparently homogeneous product, melting at 158—160°, is produced, whilst, if the aluminium chloride has been allowed to absorb a small quantity of moisture, a large quantity of pure anthraphenone melting at 148° is readily obtained. Investigation of the product of higher melting point has shown that it may be produced by crystallising anthraphenone with 3 per cent. of anthracene.

Anthraphenone, $C_{14}H_9 \cdot CPh$, crystallises from ethyl acetate in needles melting at 148°. The crystals belong to the monoclinic system [$a : b : c = 1.1704 : 1 : 0.8623$; $\beta = 94^\circ 34'$]. On oxidation with a mixture of chromic and acetic acid, it is converted into anthraquinone and benzoic acid.

Dihydroanthraphenone, $C_{14}H_{11} \cdot CPh$, made by reducing anthraphenone with zinc dust and acetic acid, crystallises from alcohol in lustrous, white needles melting at 101°. It rapidly reduces an ammoniacal solution of silver nitrate and is oxidised by chromic acid, yielding anthraquinone. It does not yield an acetyl or benzoyl derivative, and is therefore benzoyldihydroanthracene.

Nitroanthraphenone, $C_{21}H_{13}O \cdot NO_2$, crystallises from alcohol in golden-yellow needles having a metallic lustre and melting at 174°. It gives anthraquinone on oxidation, and dihydroanthraphenone and ammonia on reduction.

Tribenzoylanthracene, $C_{14}H_7Bz_3$, a bye-product in the preparation of anthraphenone, separates from nitrobenzene in yellow crystals which melt above 300°, and produces a dark red coloration with sulphuric acid. With chromic acid, it is converted into a substance which resembles anthraquinone, but melts at 255—256°; with excess of chromic acid, it gives anthraquinone and benzoic acid.

Tribenzoyltetrahydroanthracene, $C_{14}H_{11}Bz_3$, prepared by prolonged action of zinc dust and acetic acid on tribenzoylanthracene, forms yellow prisms melting at $187-188^\circ$. It does not react with acetic anhydride at high temperatures in closed tubes, so that in this substance also the carbonyl groups are intact. It reduces ammoniacal silver solutions, and is oxidised by chromic acid, yielding anthraquinone and benzoic acid.

A. L.

Thujene, a New Dicyclic Terpene. By L. TSCHUGAEFF (*Ber.*, 1900, 33, 3118—3126).—On converting thujyl alcohol into the corresponding methyl xanthate and subjecting the latter to dry distillation (compare Abstr., 1900, i, 129 and 352), *thujene*, $C_{10}H_{16}$, is obtained which boils at $151-152.5^\circ$, and has a sp. gr. 0.8275 at $20^\circ/4^\circ$ and n_D 1.45042 at 20° ; the molecular refraction is 44.21, the calculated value for a dicyclic terpene being 43.54. It fails to yield a crystalline nitroschloride, and with bromine (1 mol.) gives rise to hydrogen bromide and a reddish-brown syrup, which dissolves in alcohol with an intensely red colour. When exposed to the air, thujene is rapidly oxidised to a resin, whilst it decolorises aqueous potassium permanganate instantaneously; with hot mercuric acetate solution it yields a crystalline substance having a nacreous lustre.

From physical considerations, the new terpene appears to belong to the true thujone series, thujone itself probably having the structure assigned to it by Semmler (Abstr., 1900, i, 240); the terpene hitherto called "tanacetene" or "thujene" (Semmler, Abstr., 1893, i, 107; Wallach, *ibid.*, i, 106) probably corresponds with *isothujone* and is therefore named *isothujene* (compare Wallach, Abstr., 1895, i, 620).

W. A. D.

Formation of Terpene Derivatives in the Geranium. By EUGÈNE CHARABOT (*Compt. rend.*, 1900, 131, 806—808. Compare Abstr., 1899, i, 299; 1900, i, 241, 303; ii, 101, 361, 362).—The alcohols present in the essential oil of geranium are geraniol and rhodinol.

Two samples of the oil were obtained from the green plant, the second sample being collected one month after the first, and gave the following numbers:

| | I. | II. |
|--|----------------|-----------------|
| Sp. gr. at 15° | 0.897 | 0.899 |
| Rotatory power ($l=100$ mm.) | -10° | $-10^\circ 16'$ |
| Coefficient of saturation of the acids | 43.8 per cent. | 41.0 per cent. |
| Esters (calc. as geranyl tiglate) .. | 5.8 | 10.0 |
| Free alcohol (calc. as $C_{10}H_{18}O$) | 64.0 | 62.1 |
| Total alcohol | 67.8 | 68.6 |

The acidity and the amount of free alcohol diminish, whereas the amount of esters and total alcohol increase, during the maturation of the plant. Estimation of the amount of menthol present at different stages in the growth of the plant showed that this substance is chiefly formed in the period during which the plant possesses maximum respiratory activity.

H. R. LE S.

Neroli Oil. By HEINRICH WALBAUM (*Ber.*, 1900, **33**, 2994. Compare Abstr., 1899, i, 620, 621).—Priority is still claimed over E. and H. Erdmann (Abstr., 1900, i, 555). J. J. S.

Occurrence of Phenylethyl Alcohol in Oil of Roses. By HUGO VON SODEN and WILHELM ROJAHN (*Ber.*, 1900, **33**, 3063—3065. Compare Abstr., 1900, i, 489).—The authors point out that their discovery of the occurrence of phenylethyl alcohol in oil of roses was published before that of Walbaum (Abstr., 1900, i, 645). The investigation of two samples of French oil of roses prepared from the fresh flowers shows that 25—45 per cent. of the ethereal oil present consists of this alcohol. A small amount of the alcohol has also been found in Bulgarian oil of roses. A. H.

A New Glucoside Extracted from the Seeds of Erysimum, a Member of the Cruciferae. By FRÉDÉRIC SCHLAGDENHAUFFEN and E. REEB (*Compt. rend.*, 1900, **131**, 753—755).—The seeds of *Erysimum aureum* contain an alkaloid which causes paralysis when injected into animals and also a glucoside, erysimin, which resembles digitalin in its action on the heart. *Erysimin*, $C_4H_7O_2$, is a pale yellow, slightly hygroscopic, amorphous powder which melts at 190° and is soluble in all proportions in water and alcohol, but insoluble in ether, chloroform, benzene, or carbon disulphide. It affords the usual reactions of a glucoside. N. L.

Active Glucosides Soluble in Water contained in Frangula, Sagrada and Rhubarb. By EUGEN AWENG (*Chem. Centr.*, 1900, ii, 766—767; from *Apoth.-Zeit.*, **15**, 537—538).—*Frangula*, *Sagrada*, and *rhubarb* contain two groups of active components, consisting respectively of primary glucosides easily soluble in water and of secondary glucosides which are only slightly so. The latter are isolated by treating the residue obtained by evaporating the 70 per cent. alcoholic extract with ammonia and precipitating with acetic acid. The filtrate in each case contains the same primary glucosides, frangulic acid and a glucoside which on hydrolysis yields emodin; these compounds are easily separated by means of 96 per cent. alcohol. The emodin glucoside is almost completely precipitated from its aqueous solution by baryta, gelatin solution or formalin. Frangulic acid, from *Frangula*, *Sagrada*, or *rhubarb*, dissolves in ammonia, forming a yellow solution whilst the emodin glucoside yields an intense raspberry-red solution. The precipitate with formalin might be used to locate microscopically the position of the glucoside in the *rhubarb* rhizome. *Radix Rhapontici* was found to contain the same glucosides as *rhubarb*. The emodin glucoside is more active than frangulic acid. Since the secondary glucosides of *rhubarb* are partly soluble in hot water and on cooling separate out again, infusion of *rhubarb* should be filtered hot. E. W. W.

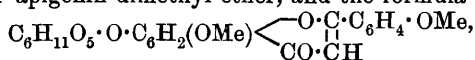
Nature and Origin of the Poison of Lotus Arabicus. By WYNDHAM R. DUNSTAN and THOMAS A. HENRY (*Proc. Roy. Soc.*, 1900, **67**, 224—226).—*Lotus Arabicus*, a leguminous plant indigenous to Egypt and Northern Africa, contains in its leaves a yellow, crystalline glucoside, *lotusin*, $C_{22}H_{19}O_{10}N$, which under the influence of an enzyme, *lotase*, also found in the plant, is hydrolysed into hydrogen cyanide,

dextrose, and a new yellow colouring matter, *lotoflavin*, $C_{15}H_{10}O_6$. The coloured product belongs to the class of phenylated pheno- γ -pyrones, and is a dihydroxychrysin isomeric with luteolin and fisetin obtained respectively from *Reseda luteola* and *Rhus cotinus*.

Lotusin and amygdalin are the only glucosides definitely known to yield hydrocyanic acid on hydrolysis. G. T. M.

Apiin. By EDUARD VONGERICHTEN (*Ber.*, 1900, 33, 2904—2909).—*Apiin methyl ether*, $C_{28}H_{30}O_{14} \cdot 2H_2O$, prepared by the action of methyl iodide and sodium methoxide on apiin, is a somewhat ill-defined product which crystallises from dilute alcohol, melts between 185° and 200° , and does not reduce Fehling's solution. It is hydrolysed by dilute hydrochloric acid to *apigenin methyl ether*, $C_{16}H_{12}O_5$, which crystallises from alcohol in minute needles and melts at 256 — 257° ; the *diacetyl* derivative forms white needles and melts at 198 — 200° ; the ether is hydrolysed by potassium hydroxide into anisic acid and phloroglucinol.

By acting on apiin with aqueous potassium hydroxide and methyl iodide, a new *glucoside* is also produced which crystallises from dilute alcohol in white needles and melts at 255° ; it is regarded as a derivative of apigenin dimethyl ether, and the formula



is suggested.

T. M. L.

Bitter Principles of Hops. By GEORG BARTH (*Chem. Centr.*, 1900, ii, 915—916; from *Zeit. ges. Brauw.*, 23, 537—542. Compare Abstr., 1900, ii, 746).—Lupulinic acid, $C_{25}H_{26}O_4$, is identical with H. Bungener's lupulinic acid, to which, however, the incorrect formula $C_{50}H_{70}O_8$ is ascribed and also with Lerner's β -bitter acid. Vlaanderen's resin, $C_{54}H_{36}O_{11} \cdot OH$, obtained by precipitating the alcoholic hop extract with water, is identical with the β -resin. When lupulinic acid is oxidised by potassium permanganate, it forms valeric acid and when heated with iodine in alkaline solution it yields iodoform. The latter reaction indicates the presence of a methoxyl group and its power of combining with bromine proves the acid to contain at least two double linkings; in Hübl's iodine addition method probably substitution also occurs. The acid character of lupulinic acid is not due to the presence of a carboxyl group, but is probably dependent on the presence of double linkings, for the acid can be removed from alkaline solutions by shaking with ether, and the bromine additive compound has neither an acid reaction nor a bitter taste; the acid is a derivative of an olefine terpene, for by melting it with potassium hydroxide an oil is obtained which, when distilled over phosphoric oxide, yields the *hydrocarbon* C_5H_8 ; it has an intense odour of leeks, similar to that of isoprene, a sp. gr. 0.8840 at 15° and n_D 1.4866 at 20° , but it does not show a constant boiling point, probably on account of polymerisation. Attempts to obtain aromatic compounds from the acid failed, but it is undoubtedly closely related to the ethereal hop oil which contains terpenes. The fact that pentosans constitute the main portion of the husks is of interest in connection with the presence of terpenes containing five carbon

atoms. The acid forms an extremely unstable compound with sulphur dioxide.

α -Lupulinic acid (α -bitter acid), which is a constituent of α -resin, is a derivative of the terpene C_5H_8 and is also related to the β -acid and to hop oil. The products obtained by melting the α - and β -acids with potassium hydroxide are similar in odour and properties. By treating the α -acid with potassium hydroxide solution and sulphuric acid, an acid, $C_{15}H_{20}O_3$, melting at $84-85^\circ$ is formed; the merest trace of this acid, when dissolved in chloroform and warmed with concentrated sulphuric acid, gives a violet coloration, but neither the α - nor the β -acid shows this reaction. The equivalent weights of the α - and β -acids are apparently nearly equal, hence the titration of the bitter principles in hops (Lintner, Abstr., 1899, ii, 264) involves no serious error. These acids are unsaturated compounds.

E. W. W.

Bismarck-Brown. By ERNST TÄUBER and FRANZ WALDER (*Ber.*, 1900, 33, 2897—2899. Compare Abstr., 1898, i, 23 and 193).—Phenylenedisazo-*m*-phenylenediamine is the most important constituent of bismarck brown, and forms from 64—71 per cent. of the commercial product. Triaminoazobenzene is sometimes formed in appreciable quantities and nitroso-*m*-phenylenediamine and aziminobenzene have also been detected as impurities. From 15 to 20 per cent. of the crude base is insoluble in benzene, and the residue insoluble in acids may amount to 7 per cent.

T. M. L.

Papaverinol. By LEO STUCHLIK (*Monatsh.*, 1900, 21, 813—830).—*Papaverinol*, $C_6H_5(OMe)_2 \cdot CH(OH) \cdot C_9NH_4(OMe)_2$, is obtained by the reduction of papaveraldine (Goldschmiedt, Abstr., 1886, 478) with zinc dust in glacial acetic acid solution; it crystallises in long, colourless, monoclinic needles [$a:b:c = 0.671:1:0.3408$; $\alpha = 116^\circ 32' 50''$], melts at 137° , forms a *hydrochloride* which melts indefinitely at 202° , yields a *platinichloride* which melts and decomposes at 168° , and has much the same physiological action as papaveraldine; the *picrate* crystallises in prismatic crystals, which melt and decompose at 171° ; the *benzoyl* compound forms yellow needles, which melt at 126° ; the *p*-*bromobenzoyl* compound melts at 194° , and the *phenylurethane* melts and decomposes at 180° . Papaverinol forms a *methiodide*, which crystallises in small, slender needles, and melts at 190° , and *additive products* with methyl chloride, ethyl bromide, and benzyl chloride which melt respectively at 182° , 172° , and 179° .

R. H. P.

Stereoisomeric 2-Phenyl-6-Methylpiperidines. By MAX SCHOLTZ and HELMUTH MÜLLER (*Ber.*, 1900, 33, 2842—2847).—The 2-phenyl-6-methylpiperidine previously described (Abstr., 1895, i, 563) is really a mixture of two isomeric bases which may be separated by conversion into their hydrochlorides and repeated treatment of these with boiling acetone; the insoluble 2-phenyl-6-methylpiperidine *hydrochloride* crystallises from water in glistening needles melting at $215-216^\circ$; the *base* obtained from it distils at $248-249^\circ$, the *platinichloride* melts at $208-209^\circ$, the *aurichloride* at $167-168^\circ$, the *hydriodide* crystallises in plates melting at $229-230^\circ$, and the *hydrobromide* also in plates melting at $180-181^\circ$.

The soluble *hydrochloride* yields a base, *iso*-2-phenyl-6-methylpiperidine, distilling at 254—258°; the *hydrobromide* does not crystallise readily, and melts at 182—183°; the *hydriodide* crystallises in colourless needles melting at 172—173°; the *platinichloride* in needles melting at 195—196°, and the *aurichloride* in plates melting at 120—121°.

Both bases are optically inactive, but are racemic compounds, as the former may be resolved by the aid of *d*-tartaric acid, and the *iso*-base by the aid of *d*-camphorsulphonic acid.

1: 2-Phenyl-6-methylpiperidine *d*-tartrate, $C_5NH_9PhMe.C_4H_6O_6.H_2O$, crystallises in hemihedral rhombic prisms [$a : b : c = 0.87352 : 1 : 1.0886$] and is less soluble than the *d*-tartrate of the *d*-base. The active *base* distils at 247—248°, and has a sp. gr. 0.9486 at 20° and $[\alpha]_D - 44.44^\circ$. The corresponding *d*-base has been isolated by the aid of *l*-tartaric acid and has a sp. gr. 0.9497 at 20° and $[\alpha]_D + 44.81^\circ$.

d-iso-2-Phenyl-6-methylpiperidine *d*-camphorsulphonate is less soluble than the salt of the *l*-base, it melts at 187—188°, and yields a *d*-base distilling at 254—256°, and having $[\alpha]_D + 0.92^\circ$. The same optically active base may be obtained directly by the addition of *d*-camphorsulphonic acid to the original mixture of the racemic bases, as the two isomeric camphorsulphonates of 2-phenyl-6-methylpiperidine do not crystallise.
J. J. S.

New Reaction of Phosgene. By [CARL] BERNHARD KÜHN [and in part W. SPINDLER and P. VON GARTZEN] (*Ber.*, 1900, 33, 2900—2904).—*o*-Acetylaminobenzylpiperidine, $NHAc.C_6H_4.CH_2.C_5NH_{10}$, prepared by the action of acetic anhydride on the base (Lellmann and Pekrun, *Abstr.*, 1891, 89) crystallises from light petroleum in small, white needles, melts at 76°, and dissolves in acids and organic solvents. Carbonyl chloride converts it into dipiperidylcarbamide (Wallach and Lehmann, *Abstr.*, 1887, 385) and *o*-acetylaminobenzyl chloride, $NHAc.C_6H_4.CH_2Cl$, which crystallises from benzene and melts at 114°.

p-Acetylaminobenzylpiperidine crystallises from benzene and light petroleum in flakes and melts at 146°; the *acetate* crystallises from benzene in small rhombic crystals and melts at 114°; the *hydrochloride* melts at 218°. *p*-Acetylaminobenzyl chloride, produced by the action of carbonyl chloride, crystallises from benzene in flat, rhombic needles and melts at 155°.

m-Acetylaminobenzylpiperidine crystallises from a mixture of benzene and light petroleum in white, glistening needles and melts at 95°. *m*-Acetylaminobenzyl chloride, produced by the action of carbonyl chloride, crystallises from a mixture of benzene and light petroleum in needles and melts at 89°.

o-Acetylaminophenylpiperidine, $NHAc.C_6H_4.C_5NH_{10}$, is an oil boiling at 340°. Carbonyl chloride converts it into the chloroimide, which combines with aniline, forming *diphenylpiperidylethenylamidine*, $NHPh.CMe.N.C_6H_4.C_5NH_{10}$; this crystallises from alcohol in brown needles, melts at 135°, and yields a crystalline *hydrochloride*, *picrate*, and *platinichloride*.
T. M. L.

Organic Bases of Russian Petroleum. By GRIGORI V. CHLOPIN (*Ber.*, 1900, 33, 2837—2841).—Caucasian petroleum contains about

0.005—0.006 per cent. of pyridine bases of the general formula $C_nH_{2n-15}N$. Six different fractions of the bases have been obtained by the aid of their platinichlorides, but whether the six fractions are homogeneous is questionable. The molecular weights of the different fractions lie between 104 and 308; the most complex fraction gives numbers which agree with those required for the formula $C_{22}H_{29}N$ for the base and $(C_{22}H_{29}N)_2 \cdot H_2PtCl_6$ for the platinichloride. The bases are poisonous in their action on fish, but not on white rats or cats. They do not possess disinfecting properties. J. J. S.

Condensation of Cyanoacetamide with Chloroform. By GIORGIO ERRERA (*Ber.*, 1900, 33, 2973—2976.)—From Guthzeit's researches (*Abstr.*, 1899, i, 450), it is probable that the compounds previously described (*Abstr.*, 1898, i, 298) as α - γ -dicyanoglutaconamide and α -carbonamido- γ -cyanoglutaconic acid are respectively the ammonium derivatives of 3:5-dicyano-2:6-dihydroxypyridine, $OH \cdot C_5NH(CN)_2 \cdot O \cdot NH_4$, and of 5-cyano-2:6-dihydroxypyridine-3-carboxylamide, $OH \cdot C_5NH_5(CN)(CO \cdot NH_2) \cdot O \cdot NH_4$, or their ketonic tautomerides. The former compound may be crystallised from hydrochloric acid of sp. gr. 1.1, or boiled with aqueous sodium hydroxide (1 equivalent) without decomposition. Both compounds, when boiled with a large excess of alkali, are decomposed into a mixture of products. It appears that these substituted pyridines are very strongly acidic, being comparable with mineral acids.

The monoamide of 2:6-dihydroxypyridine-3:5-dicarboxylic acid, $CO_2H \cdot C_5NH(OH)_2 \cdot CO \cdot NH_2$, obtained by boiling the above carbonamidopyridine with excess of alkali, crystallises in needles melting and decomposing at 213°. J. J. S.

Mixed Methenyl Compounds. III. Action of Ethyl Ethoxymethylenacetoacetate on Cyanoacetamide. By GIORGIO ERRERA (*Ber.*, 1900, 33, 2969—2973. Compare *Abstr.*, 1900, i, 33.)—Ethyl 5-cyano-6-hydroxy-2-picoline-3-carboxylate, $OH \cdot C_5NHMe(CN) \cdot CO_2Et$, obtained in the form of its sodium derivative by the action of ethyl ethoxymethylenacetoacetate on the sodium derivative of cyanoacetamide, is best purified by conversion into its potassium derivative, $C_{10}H_9O_3N_2K$, which crystallises in colourless plates readily soluble in water, but only sparingly so in alcohol. The ester crystallises from alcohol in glistening plates, and when hydrolysed with concentrated sulphuric acid or aqueous potash yields 6-hydroxy-5-carboxylamido-2-picoline-3-carboxylic acid, $OH \cdot C_5NHMe(CO \cdot NH_2) \cdot CO_2H$, which separates from boiling water as a colourless, crystalline powder turning black at 300°. 6-Hydroxy 2-picoline-3:5-dicarboxylic acid, obtained by hydrolysing the amide with hydrochloric acid of sp. gr. 1.1 at 120°, crystallises in needles or plates containing $1H_2O$, which it readily loses at 100°, and then melts at 303°. 6-Hydroxy-2-picoline, $C_5NH_3Me \cdot OH$, is formed when the dibasic acid is heated with hydrochloric acid for a short time at 130°; it crystallises in glistening needles containing 4 or $5H_2O$, which it loses on exposure to air; the anhydrous base crystallises from benzene in thick crystals melting at 159° and readily soluble in alcohol. The hydrochloride contains water of crystallisation and melts

at 80—85°, the *platinichloride* dissolves readily in ether, alcohol, or water.

3:5-Dibromo-6-hydroxy-2-picoline, $C_5NHBr_2Me \cdot OH$, obtained when the aqueous solution of the base is treated with bromine water, crystallises in needles melting at 238—239°.

Attempts to obtain ethyl malonomethylenacetate have proved unsuccessful, as a mixture of ethyl methylenbisacetate and ethyl dicarboxylglutaconate is formed. J. J. S.

Hydrindene. By JULIUS DÜNKELSBÜHLER (*Ber.*, 1900, 33, 2895—2897).—*Nitrohydroxyhydrindene*, $C_9H_9O_3N$, prepared by the action of cold dilute nitric acid on hydrindene, crystallises from dilute alcohol, melts at 40°, and is volatile in steam. *Aminohydroxyhydrindene*, $C_9H_{11}ON$, forms colourless, glistening needles and melts and decomposes at 184°. Hydrindene has also been nitrated, but the nitro-derivatives are not described. T. M. L.

Dihydroisoindole (o-Xylylenimine). By KURT FRÄNKEL (*Ber.*, 1899, 33, 2808—2818).—Phthalazonecarboxylic acid gives a sparingly soluble *ammonium* salt, $C_9H_{11}O_4N_3$, which crystallises in beautiful, white prisms melting at 237°. *Phthalazonecarboxylic chloride*, $C_9H_5O_2N_2Cl$, crystallises in dry benzene in white needles, sinters at 183°, and melts at 186°. *Ethyl phthalazonecarboxylate*, $C_9H_5O_8N_2Et$, forms beautiful, felted needles melting at 169°.

5-Nitrodihydroisoindole, $NO_2 \cdot C_6H_3 \begin{smallmatrix} <CH_2 \\ >CH_2 \end{smallmatrix} NH$, made by adding fuming nitric acid to a solution of dihydroisoindole in sulphuric acid, is oily, but yields crystalline salts. It is converted into 4-nitrophthalic acid by oxidation with potassium dichromate and sulphuric acid. The *hydrochloride*, $C_8H_8O_2N_2 \cdot HCl$, forms white needles and melts above 250°; the *sulphate* crystallises in needles and melts at 240—260°; the *nitrate*, $C_8H_8N_2O_2 \cdot HNO_3$, forms quadratic prisms which melt and decompose at 158°. The *nitrosoamine*, $NO_2 \cdot C_8H_7N \cdot NO$, forms brownish-yellow prisms melting at 168—169°. 4-Nitrophthalimide, $NO_2 \cdot C_6H_3 : C_2O_2 : NH$, forms white needles which melt at 193—195°.

5-Aminodihydroisoindole, $NH_2 \cdot C_8NH_8$, is obtained by reducing the nitro-compound with stannous chloride; its *picrate*, $C_8H_{10}N_2 \cdot C_6H_3O_7N_3$, forms yellow needles which melt at 203—204°.

Benzoyldihydroisoindole, C_8NH_8Bz , obtained from dihydroisoindole by the Baumann-Schotten reaction, is readily soluble in alcohol, benzene, and toluene, and separates from light petroleum in rose-coloured, quadratic tablets melting at 100°.

o-Xylylenehydrazine, $C_6H_4 \begin{smallmatrix} <CH_2 \\ >CH_2 \end{smallmatrix} N \cdot NH_2$, prepared from the nitrosoamine by treatment with zinc dust and dilute acetic acid, is a brownish oil which absorbs carbon dioxide from the air and reduces warm Fehling's solution. The *hydrochloride*, $C_8H_8N \cdot NH_2 \cdot HCl$, forms white needles and melts at 190—194°. The *picrate*,

$C_8H_8N \cdot NH_2 \cdot C_6H_3N_3O_7 \cdot \frac{1}{2}H_2O$, crystallises in long, yellow needles, melting at 96—97°. *Benzylidene-o-xylylenehydrazine*, $C_8H_8N_2 \cdot CHPh$, crystallises from alcohol in pearly

leaflets melting at 127—129°. *o*-Hydroxybenzylidene-*o*-xylylenehydrazine, $C_8H_8N_2 \cdot CH \cdot C_6H_4 \cdot OH$, forms glistening leaflets melting at 165—166°.

Dihydroisoindylphenylthiocarbamide, $NHPh \cdot CS \cdot NC_8H_8$, crystallises from toluene in white leaflets melting at 226—227°. *Dihydroisoindylallylthiocarbamide* forms white needles melting at 138—139°; when heated with hydrochloric acid, it yields *propylenedihydroisoindyl-ψ-thiocarbamide*, $C_6H_4 \begin{smallmatrix} CH_2 \\ < \\ CH_2 \end{smallmatrix} N \cdot C \begin{smallmatrix} S-CHMe \\ < \\ N \cdot CH_2 \end{smallmatrix}$, which crystallises from ethyl acetate in long, white needles melting at 78—80°.

Dimethyldihydroisoindylum iodide, $C_8NH_8Me_2I$, prepared from dihydroisoindole and methyl iodide, forms shining leaflets and melts and darkens at 244—245°. The *platinichloride*, $(C_{10}H_{13}N)_2 \cdot H_2PtCl_6$, forms orange needles melting at 225°; the *picrate*, large needles melting at 145°; and the *aurichloride* yellow needles melting at 178°. The base absorbs carbon dioxide from the atmosphere and decomposes on distillation, yielding 2-methyldihydroisoindole, C_8NH_8Me . This boils at 205—215°, has an odour resembling that of train oil, and becomes coloured on exposure to the air; the *platinichloride*, $(C_9H_{11}N)_2 \cdot H_2PtCl_6$, forms brownish-yellow prisms melting at 200—201°.

2-γ-Methoxypropyldihydroisoindole, $C_8NH_8 \cdot C_3H_6 \cdot OMe$, from dihydroisoindole and methoxychloropropane, boils at 269—273°, and yields a solid *aurichloride*, $C_{12}H_{17}ON \cdot HAuCl_4$.

2-γ-Phenoxypropyldihydroisoindole, $C_8NH_8 \cdot C_3H_6 \cdot OPh$, crystallises from well-cooled light petroleum in nodular aggregates of white needles melting at 57—58°; the *aurichloride*, *platinichloride*, and *picrate* could not be obtained in a crystallised form.

2-γ-Bromopropyldihydroisoindole, $C_8NH_8 \cdot C_3H_6Br$, made by heating the foregoing phenoxy-compound with fuming hydrobromic acid at 100°, forms a yellow oil; the *hydrobromide*, $C_{11}H_{15}NBr_2$, forms white needles melting at 155—156°, and the *picrate*, $C_{17}H_{17}O_7N_4Br$, yellow needles and melts at 129—131°.

o-Nitrobenzylidihydroisoindole, $C_8NH_8 \cdot CH_2 \cdot C_6H_4 \cdot NO_2$, crystallises from alcohol in yellow needles which melt at 80—81°; on reduction, it yields *o*-aminobenzylidihydroisoindole, $C_8NH_8 \cdot CH_2 \cdot C_6H_4 \cdot NH_2$, which forms yellowish needles melting at 98—100°.

p-Nitrobenzylidihydroisoindole separates from alcohol in brownish-yellow needles and melts at 78—80°. A. L.

3-Nitroindoles. By ANGELO ANGELI and FRANCESCO ANGELICO (*Gazzetta*, 1900, 30, ii, 268—283).—The position of the nitroso-group in the 3-nitrosoindoles is fixed by their behaviour on oxidation; thus, with alkaline permanganate, 3-nitroso-2-phenylindole yields benzoyl-anthranilic acid. On oxidation, the nitrosoindoles behave similarly to the nitrosophenols and yield the corresponding nitroindoles, which cannot be obtained by direct nitration of the indoles, as in this way polynitro-derivatives are always obtained; with nitrosoindoles containing an aliphatic radicle, the oxidation takes place best in alkaline solution, whilst if an aromatic substituent be present, acid and alkaline oxidation yield equally good results.

3-Nitro-2-phenylindole, $\text{NH} \langle \text{C}_6\text{H}_4 \rangle_{\text{CPh}} \text{C} \cdot \text{NO}_2$, separates from acetic acid in lustrous, yellow crystals melting and decomposing at 238—239°. Oxidation of this compound and also of the corresponding nitroso-derivative yields benzoylanthranilic acid, which when heated with acetic anhydride, gives rise to an *anhydride*, $\text{C}_6\text{H}_4 \langle \text{C} \rangle_{\text{NBz}}$, or $\text{C}_6\text{H}_4 \langle \text{C} \rangle_{\text{N}=\text{CPh}}$, separating from light petroleum in white crystals melting at 122—123°.

3-Nitro-2-phenyl-1-ethylindole, $\text{NEt} \langle \text{C}_6\text{H}_4 \rangle_{\text{CPh}} \text{C} \cdot \text{NO}_2$, crystallises from alcohol in yellow needles melting at 175°.

3-Nitro-2-methylindole, $\text{C}_9\text{H}_8\text{O}_2\text{N}_2$, separates from dilute alcohol in shining, yellow scales with an azure surface colour melting at 237°.

Dinitro-2-phenylindole, $\text{NH} \langle \text{C}_6\text{H}_3(\text{NO}_2) \rangle_{\text{CPh}} \text{C} \cdot \text{NO}_2$, obtained by mixing a hot acetic acid solution of the phenylindole with the calculated quantity of sodium nitrite and adding a large excess of concentrated nitric acid, crystallises from alcohol in yellow scales melting above 280°. Dinitro-2-phenyl-1-ethylindole, $\text{C}_{16}\text{H}_{13}\text{O}_4\text{N}_3$, separates from alcohol in sparkling, golden-yellow needles melting at 221°; on treatment with alcoholic potassium hydroxide, it gives the *azoxy*-compound of the constitution $\text{ON}_2 \left(\text{C}_6\text{H}_3 \langle \text{C}(\text{NO}_2) \rangle_{\text{NEt}} \text{CPh} \right)_2$, which does not melt at 285° and is insoluble in all solvents. With hydroxylamine hydrochloride in presence of sodium ethoxide, dinitro-2-phenyl-1-ethylindole yields an unstable oxime which is soluble in alkali solutions and has all the properties of a nitrohydroxylamine. T. H. P.

Iodo-derivatives of Quinoline, *iso*Quinoline, and 1-Methylquinoline. By ALBERT EDINGER and A. SCHUMACHER (*Ber.*, 1900, 33, 2886—2892).—Triiodoquinoline, obtained by heating a mixture of quinoline, iodine, and fuming sulphuric acid containing 50 per cent. of trioxide for 5—6 hours at 100°, separates from benzene in stout, yellow crystals and from alcohol in nearly white needles; it melts at 189°, sublimes at 290°, and yields a yellow, crystalline *sulphate*, *hydrochloride*, and *platinichloride*, but fails to give a methiodide. Hot fuming nitric acid converts it into a diiodonitroquinoline, which crystallises from alcohol, or sublimes, in bright yellow needles and melts at 203°. The same compound is obtained, together with a crystalline triiodonitroquinoline, melting at 270°, on attempting to oxidise triiodoquinoline by heating for 2 hours at 210° with nitric acid of sp. gr. 1.12.

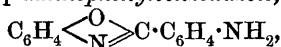
Triiodoisoquinoline, obtained in similar manner to triiodoquinoline, crystallises from alcohol in bright brown needles, melts at 253° and yields a yellow, crystalline *chloride*, *sulphate*, *nitrate*, and *platinichloride* (with $\frac{1}{2}\text{H}_2\text{O}$); the *methiodide* crystallises from water in bright yellow needles and decomposes at 280—285°. Fuming nitric acid at 100° converts triiodoisoquinoline into diiodonitroisoquinoline, which crystallises from glacial acetic acid in yellow needles and melts at 208°. Diiodoisoquinoline is a bye-product in the preparation of triiodoisoquinoline,

especially when fuming sulphuric acid containing more than 50 per cent. of trioxide is employed; it crystallises from alcohol or xylene in white needles and melts at 151° , and yields a *platinichloride*, with $\frac{1}{2}\text{H}_2\text{O}$, which melts and decomposes at 300° .

When 1-methylquinoline is treated with iodine in the same way as quinoline and isoquinoline, it yields a *diiodo-1-methylquinoline* along with its *monosulphonic acid*; the former crystallises from xylene in white needles, melts at 171° , and yields a yellow, crystalline *hydrochloride*, *sulphate*, *nitrate*, and *platinichloride* (with $\frac{1}{2}\text{H}_2\text{O}$), whilst the latter crystallises from water, decomposes at 270° , and gives a crystalline *barium salt* with $1\frac{1}{2}\text{H}_2\text{O}$. The formation of the sulphonic acid is obviated by using fuming sulphuric acid containing more than 50 per cent. of trioxide. *Diiodonitro-1-methylquinoline* crystallises from alcohol and melts at 206° .

W. A. D.

Benzazoles and Dyes derived from them. By OTTO KVM (*Ber.*, 1900, **33**, 2847—2851. Compare Abstr., 1899, i, 674, 941; 1900, i, 190).—*o-Nitrophenyl-p-nitrobenzoate*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, crystallises from acetone in glistening plates melting at $139\text{--}140^{\circ}$, and when reduced yields 1-*p-aminophenylbenzoxazole*,



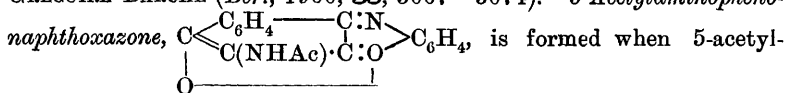
which crystallises in reddish-white needles melting at $173\text{--}174^{\circ}$.

p-Nitrobenzoyl-o-nitroaniline is sparingly soluble in the usual solvents and melts at $219\text{--}220^{\circ}$. On reduction, it yields 2-*p-aminophenylbenziminazole*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagdown \text{N} \end{array} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, melting at $235\text{--}236^{\circ}$ and yielding deep violet fluorescent solutions.

These two compounds and those previously described have been diazotised and combined with β -naphtholdisulphonic acid and with α -naphthol, and the dyes thus obtained tested on cotton. The position of the azo-group in the benzazoles appears to have little influence on the readiness with which the cotton takes up the dye, but those with the azo-group in the α -phenyl ring dye more intensely than their isomerides, and the dyes also exhibit a deeper bluish tone. When azo-groups are present in both rings, the tone is deepened enormously and the fabric is dyed much more readily.

J. J. S.

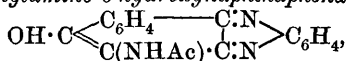
Syntheses of Oxazine and Azine Derivatives by Means of Acetaminonaphthalic Acid. By FRIEDRICH KEHRMANN and GREGOIRE BACHE (*Ber.*, 1900, **33**, 3067—3074).—5-*Acetylaminophenonaphthoxazone*,



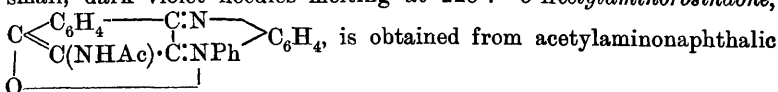
aminonaphthalic acid is heated with *o*-aminophenol and acetic acid, and crystallises in orange-yellow needles which decompose at about 310° . On hydrolysis, it yields 5-aminophenonaphthoxazone, which crystallises in slender, dark red needles melting at $211\text{--}212^{\circ}$, and is identical with the compound previously obtained by the nitration of phenonaphthoxazone and the reduction of the product, so that the constitution of this substance is thus established (Abstr., 1898, i, 45). 2-*Nitro-5-acetyl-*

aminophenonaphthoxazone, $\text{C} \begin{array}{c} \text{C}_6\text{H}_4 \text{---} \text{C}:\text{N} \cdot \text{C}:\text{CH} \cdot \text{C} \cdot \text{NO}_2 \\ \text{C}(\text{NHAc}) \cdot \text{C}:\text{O} \cdot \text{C}:\text{CH} \cdot \text{CH} \end{array}$, is obtained

from 4-nitro-*o*-acetylaminophenol, and crystallises in light, reddish-brown needles. The *base*, obtained by hydrolysis, crystallises in black, lustrous plates melting at 288°, and on reduction yields 2 : 5-diaminophenonaphthoxazone, $\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_3$, which crystallises in dark violet needles with a coppery lustre, and melts at 308°. The *diacetyl* derivative forms brick-red needles. 5-Acetylamino-6-hydroxynaphthaphenazine,

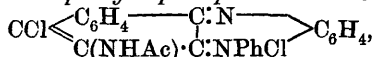


formed when acetylaminonaphthalic acid is heated with *o*-phenylenediamine and acetic acid, melts at 257—258°. The *base* crystallises in small, dark violet needles melting at 225°. 5-Acetylaminorosindone,



acid and *o*-aminodiphenylamine, and forms garnet-red needles melting at 249—250°. 5-Aminorosindone forms long, dark blue needles which resemble those of indigo, and melt at 215—216°. Attempts to prepare an *isorosinduline*, $\text{CH} \begin{array}{c} \text{C}_6\text{H}_4 \text{---} \text{C}:\text{N} \\ \text{C}(\text{NH}_2) \cdot \text{C}:\text{NClPh} \end{array} > \text{C}_6\text{H}_4$, from the acetyl derivative have hitherto proved unsuccessful.

6-Chloro-5-acetylaminophenyl-naphthaphenazonium chloride,



is prepared by the action of phosphorus pentachloride on acetylaminorosindone dissolved in phosphorus oxychloride, and is an orange-red, crystalline powder, the *platinichloride* being a bright red, crystalline precipitate. The *bromide* is precipitated by sodium bromide from the aqueous solution of the chloride, and closely resembles the latter. Aniline converts the chloride into 5-acetylaminophenylrosinduline chloride, $\text{NHPh} \cdot \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \text{---} \text{C}:\text{N} \\ \text{C}(\text{NHAc}) \cdot \text{C}:\text{NPhCl} \end{array} > \text{C}_6\text{H}_4$, which rapidly passes

into an *iminazole* derivative, $\text{CMe} \begin{array}{c} \text{NPh} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{C}:\text{N} \\ \text{N} \text{---} \text{C} \text{---} \text{C}:\text{NPhCl} \end{array} > \text{C}_6\text{H}_4$, crystallising in thick, dark brown, lustrous prisms; the *platinichloride* is a dark red, crystalline precipitate.

A. H.

Action of Bromonitrobenzenes on *p*-Phenylenediamine. By ERNST BANDROWSKI (*Chem. Centr.*, 1900, ii, 852; from *Bull. Acad. Sci. Cracow*, 1900, 186—193).—*p*-Phenylenediamine does not act on *m*-bromonitrobenzene, but it slowly attacks *o*- and *p*-bromonitrobenzene, forming only nitrophenyl-*p*-phenylenediamine and not dinitrodiphenyl-*p*-phenylenediamine. *p*-Nitrophenyl-*p*-phenylenediamine hydrochloride, prepared by means of hydrochloric acid from the product obtained by heating a mixture of *p*-phenylenediamine, *p*-bromonitrobenzene, and sodium acetate in the mol. proportions 2 : 1 : 1 respectively (1 : 2 : 1 ?) with alcohol at 160—170°, separates from dilute hydrochloric

acid in yellow crystals and loses hydrogen chloride on exposure to the air or more quickly by boiling with water.

p-Nitrophenyl-*p*-phenylenediamine, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, obtained from the hydrochloride by the action of ammonia, forms cherry-red, iridescent crystals, which have a metallic lustre, melts at $211-212^\circ$, and is slightly soluble in the ordinary solvents.

Acetyl-p-nitrophenyl-p-phenylenediamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, separates from alcohol in yellow crystals and melts at 22° . *p*-Nitrophenylethyl *p*-phenylenediamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHEt}$, prepared by warming *p*-nitrophenyl-*p*-phenylenediamine with ethyl iodide (1 mol.) in alcoholic solution, separates in dark red crystals and melts at $146-149^\circ$. By the action of benzaldehyde on *p*-nitrophenyl-*p*-phenylenediamine, *p*-nitrophenylbenzylidene-*p*-phenylenediamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CHPh}$ is obtained; it crystallises from alcohol in golden-yellow needles, melts at 219° and is sparingly soluble in alcohol. Di-*p*-diaminodiphenylamine, $\text{NH}(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_2$, is formed by the action of tin and hydrochloric acid on nitrophenyl-*p*-phenylenediamine.

Di-*p*-dibromoazobenzene, melting at 205° , and other products are also formed in the original reaction.

o-Nitrophenyl-*p*-phenylenediamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, prepared from *o*-bromonitrobenzene, crystallises in nearly black, pointed crystals which have a metallic lustre, melts at $105-106^\circ$, is rather easily soluble in hot alcohol and forms crystalline, orange-yellow salts. The hydrochloride crystallises in aggregates of needles. *Acetyl-o-nitrophenyl-p-phenylenediamine* crystallises from alcohol in dark red leaflets, and melts at $135-136^\circ$. *o*-Nitrophenylbenzylidene-*p*-phenylenediamine forms dark red crystals and melts at $98-99^\circ$.

o-*p*-Diaminodiphenylamine is formed by reducing nitrophenylphenylenediamine, but could not be isolated.

E. W. W.

Stereochemistry of Nitrogen : Stereoisomeric Hydrazones of Ethyl Pyruvate. By L. J. SIMON (*Compt. rend.*, 1900, 131, 682-684).—The action of phenylhydrazine on ethyl pyruvate in presence of alcohol yields two phenylhydrazones, identical in composition, molecular weight, and behaviour with reagents, but differing in melting point and solubility in organic solvents. One, which is formed in much the larger proportion, and is the less soluble, melts at $118-120^\circ$, whilst the other melts at $31-32^\circ$.

C. H. B.

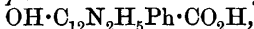
Action of Urethane on Aromatic Diamines. By C. MANUELLI and V. RECCHI (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 269-272).—With ethylurethane, *o*-, *m*-, and *p*-phenylenediamines yield respectively *o*-, *m*-, and *p*-phenylenecarbamides. By treating the latter with an excess of phosphorus pentachloride and a few drops of oxychloride, the corresponding *chlorobenziminazoles*, $\text{C}_7\text{H}_5\text{N}_2\text{Cl}$, are obtained; that obtained from *o*-phenylenecarbamide separates from aqueous alcohol as a white powder, which becomes brown on exposure to light, and melts at about 215° ; the compound from *m*-phenylenecarbamide is white, but is turned brown by light, and does not melt definitely, but decomposes at about 200° ; from *p*-phenylenecarbamide a compound was obtained which could not be purified.

T. H. P.

3-Phenyl- and 3-Methyl-4:7-quinolino-2-carboxylic Acids and their Derivatives. By CONRAD WILLGERODT and SIEGFRIED JABLONSKI (*Ber.*, 1900, **33**, 2918—2928. Compare *Chem. Zeit.*, 1900, **24**, 311, 437).—The authors have applied Doebner's method (*Abstr.*, 1887, 504) to 6-aminoquinoline, and have thus obtained a number of substituted derivatives of 4:7-quinolino [ψ-phenanthroline].

3-Phenyl-ψ-phenanthroline-2-carboxylic acid, $C_{12}N_2H_6Ph \cdot CO_2H$, obtained by the action of pyruvic acid and benzaldehyde on 6-aminoquinoline in alcoholic solution, is a yellowish, microcrystalline powder melting at 290° ; it does not form additive compounds with alkyl haloids, but yields salts, both with acids and bases. The *sodium*, *potassium*, and *barium* salts crystallise in needles, whilst the *copper* and *silver* salts are amorphous and insoluble. The *platinichloride* is a brown, crystalline precipitate; the *nitrate*, $C_{19}H_{12}O_2N_2 \cdot 2HNO_3$, crystallises in yellow plates, and the *hydrogen sulphate* forms pink cubes. The *methyl ester*, prepared from the silver salt, crystallises in colourless needles melting at 158° ; the *ethyl ester* melts at 146° , and forms an *ethiodide*, melting at 225° . On nitration, the acid yields the 6-nitro-derivative, $NO_2 \cdot C_{12}N_2H_5Ph \cdot CO_2H$, which melts at 310° , and on reduction is converted into the corresponding 6-amino-acid melting at 293° ; the *platinichloride*, $C_{19}H_{13}O_2N_3 \cdot H_2PtCl_6$, is a crystalline powder.

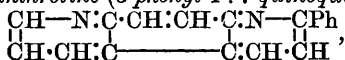
6-Hydroxy-3-phenyl-ψ-phenanthroline-2-carboxylic acid,



obtained from the amino-acid by means of the diazo-reaction, is a crystalline powder, insoluble in indifferent solvents, but readily soluble in dilute alkalis. The 6-chloro-acid, $C_{19}H_{11}O_2N_2Cl$, is also prepared from the amino-acid and is a crystalline powder melting at 289° . The corresponding bromo-acid melts at 283° , and the iodo-acid at 272° . The bromo-acid is identical with that prepared from 8-bromo-6-aminoquinoline by the action of benzaldehyde and pyruvic acid, and hence both it and the amino- and nitro-compounds from which it has been obtained must have the constitution which has been assigned to them.

ψ-Phenanthroline-1:3-dicarboxylic acid, $C_{12}N_2H_6(CO_2H)_2$, obtained by the oxidation of phenyl-ψ-phenanthrolinecarboxylic acid with potassium permanganate, is a white powder melting at 248° ; the *silver* salt is an amorphous white precipitate.

3-Phenyl-ψ-phenanthroline (3-phenyl-4:7-quinolino),

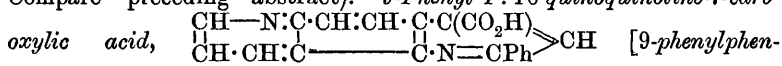


is formed when sodium phenyl-ψ-phenanthrolinecarboxylate is distilled with soda-lime, and crystallises in white plates melting at 183° . The *platinichloride* is a grey, crystalline precipitate, and the *methiodide* crystallises in lustrous yellow needles melting at 242° . 6-Nitro-3-phenyl-ψ-phenanthroline is formed by the direct nitration of phenyl-ψ-phenanthroline and is also formed when sodium nitrophenyl-ψ-phenanthrolinecarboxylate is heated with soda-lime; it forms yellow crystals melting at 281° and on reduction yields the 6-amino-compound which crystallises in greenish plates melting at 222° . 6-Hydroxy-3-phenyl-ψ-phenanthroline is a yellowish-red, crystalline powder melting at 168° . 3-Phenyl-ψ-phenanthroline-6-sulphonic acid, $C_{12}N_2H_6Ph \cdot SO_3H$,

is prepared by the sulphonation of phenyl- ψ -phenanthroline and forms a green, microcrystalline powder melting above 350°.

3-Methyl- ψ -phenanthroline-2-carboxylic acid, $C_{12}N_2H_6Me \cdot CO_2H$, prepared from aminoquinoline, pyruvic acid, and paraldehyde, is a deep red, microcrystalline powder which melts at 205°. The sodium salt crystallises in slender, light-yellow, hygroscopic needles, whilst the copper salt is amorphous. The *platinichloride*, $(C_{14}H_{10}O_2N_2)_2, H_2PtCl_6$, is formed when the acid is added to alcoholic platinum chloride, whilst another salt, $C_{14}H_{10}O_2N_2, H_2PtCl_6$, is produced by adding platinum chloride to a solution of the acid in hydrochloric acid. The *hydrogen sulphate* crystallises in light yellow, transparent needles. **3-Methyl- ψ -phenanthroline**, $C_{12}N_2H_7Me$, crystallises in silky needles melting at 88°, and forms a crystalline *platinichloride*, a *methiodide* melting at 257°, and an *ethiodide* melting at 239°. A. H.

9-Phenyl-4:10-quinolino-7-carboxylic Acid and 9-Methyl-4:10-quinolino-7-carboxylic Acid. By CONRAD WILLGERODT and ERWIN VON NEANDER (*Ber.*, 1900, 33, 2928—2935. Compare preceding abstract).—**9-Phenyl-4:10-quinolino-7-carboxylic acid**,



is prepared from 5-aminoquinoline, and forms yellow, microcrystalline needles melting at 353—355°; the sodium, potassium, and ammonium salts are soluble and crystalline, whilst the copper and silver salts are insoluble and amorphous. The *hydrochloride*, *nitrate*, and *hydrogen sulphate* are all crystalline salts, readily decomposed by water, and the *platinichloride* forms very small, reddish needles. The *methyl ester* melts at 158°, and forms a *methiodide* melting at 262°; the *ethyl ester* melts at 116°. **5-Nitro-9-phenylphenanthroline-7-carboxylic acid**, $C_{19}H_{11}O_4N_3$, is a light yellow, microcrystalline powder melting at 285°; the corresponding *amino-derivative* melts at 302—303° and forms a *platinichloride*, $(C_{19}H_{13}O_2N_3)_2, H_2PtCl_6$. **5-Chloro-9-phenylphenanthroline-7-carboxylic acid** melts at 278°, and the corresponding *bromo-acid* at 286—288°. The latter can also be prepared directly from 8-bromo-5-aminoquinoline. Phenylphenanthrolinecarboxylic acid is converted by sulphonation into a *sulphonic acid*, $C_{19}H_{11}O_2N_2(SO_3H)$, decomposing at 310°, the position of the sulphonic acid group in which has not yet been ascertained. **5-Hydroxy-9-phenylphenanthroline-7-carboxylic acid** cannot be prepared from the amino-acid, but may be obtained by synthesis from 8-hydroxy-5-aminoquinoline; it is a yellow, microcrystalline powder melting at 293°. **9-Phenylphenanthroline**, $C_{12}N_2H_7Ph$, is obtained from the carboxylic acid, and crystallises in compact white needles melting at 129°. The *platinichloride* is a reddish powder. **5-Nitro-9-phenylphenanthroline** melts at 218°, and the corresponding *amino-compound* at 232°. This base forms two *platinichlorides*, $(C_{18}H_{13}N_3)_2, H_2PtCl_6$ and $(C_{18}H_{13}N_3)_2, 3H_2PtCl_6$.

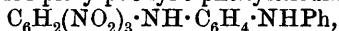
9-Phenylphenanthroline readily yields a *sulphonic acid*, $C_{18}H_{11}N_2 \cdot SO_3H$, which decomposes at 250°.

9-Methylphenanthroline-7-carboxylic acid, $C_{14}H_{10}O_2N_2$, melts at

309—310°, and yields a *sodium* salt which is more readily soluble in water than that of the corresponding phenyl derivative. A. H.

Thiopyrine. By AUGUST MICHAELIS and H. BINDEWALD (*Ber.*, 1900, 2873—2874).—5-Chloro-1-phenyl-3-methylpyrazole methiodide, which with alcoholic potash yields antipyrine (*Abstr.*, 1899, i, 941), with alcoholic potassium hydrogen sulphide gives rise to *thioantipyrine* (*thiopyrine*), $C_{10}H_{12}N_2S$; this forms colourless, tabular crystals, melts at 166°, and yields a crystalline *hydrochloride*. The author considers the compound obtained by Silberstein (German Patent, 1899, 113384) from aniline, antipyrine, and phosphorus oxychloride to have the formula, $C_{10}H_{12}N_2 \cdot NPh$, analogous to thiopyrine, 5-chloro-1-phenyl-3-methylpyrazole methochloride being probably formed initially in this case. W. A. D.

Preparation and Reactions of isoPhenosafrafranine. By FRIEDRICH KEHRMANN and OTTO KRAMER (*Ber.*, 1900, 33, 3074—3081. Compare *Abstr.*, 1900, i, 61).—Picryl chloride reacts with *o*-aminodiphenylamine to form picrylphenyl-*o*-phenylenediamine,



which crystallises in lustrous, garnet-red plates and at 120° loses nitrous acid, forming dinitrophenyldihydrophenazine. *isoPhenosafrafranine* is best prepared by reducing picrylphenyl-*o*-phenylenediamine with the calculated amount of stannous chloride in presence of alcohol and hydrochloric acid. Sulphuric acid converts *isophenosafrafranine* into *isosafraninone*, $C_{18}H_{13}ON_3$, which crystallises in blackish-brown needles and melts and decomposes at 310—315°. The *chloride* crystallises in brown, lustrous needles, and the *nitrate* in blackish-brown needles.

The stannochloride of leuco*isosafranin* yields on treatment with acetic anhydride an *acetyl* derivative which rapidly oxidises, forming *monoacetylisophenosafrafranine*, the *chloride* of which, $C_{20}H_{17}ON_4Cl$, crystallises in violet-brown needles with a bronze lustre, whilst the *platinichloride* is a dark-red, microcrystalline precipitate. Acetic anhydride converts the chloride into the chloride of a *diacetyl* derivative, crystallising in needles with a bronze lustre. When a solution of the stannochloride of leuco*isophenosafrafranine* is treated with sodium carbonate, ammonia, or aniline, the liquid becomes magenta-red on standing, owing to the production of *aposafranin*, ammonia being eliminated in considerable quantity. Since this substance can readily be converted into phenosafrafranine, this series of reactions provides a means of synthesising the latter important compound from picryl chloride and *o*-aminodiphenylamine. A. H.

Relationship between the Constitution and Colour of Isomerides of Rosinduline. By FRIEDRICH KEHRMANN (*Chem. Centr.*, 1900, ii, 813—814; from *Arch. Sci. phys. nat. Genève*, [iv], 10, 97—111. Compare *Abstr.*, 1898, i, 154, 155; 1899, i, 238, 525; 1900, i, 60).—The alcoholic solutions of the amino-derivatives of phenylnaphthaphenazonium and phenylisonaphthaphenazonium absorb much more light than those of the original compounds. The compounds which contain the amino-group in the para-position in regard

to the quaternary nitrogen atom, as, for instance, 10-amino-7-phenyl-naphthaphenazonium 7-chloride, $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{NPhCl} \end{smallmatrix} > C_6H_5 \cdot NH_2$, are blue whilst those, on the other hand, in which the amino-group is in the para-position to the tertiary nitrogen atom, such as 5-amino-7-phenyl-naphthaphenazonium 7-chloride, $NH_2 \cdot C_{10}H_5 \begin{smallmatrix} \text{N} \\ \text{NPhCl} \end{smallmatrix} > C_6H_4$, are red. The derivatives containing the amino-group in the other or non-quinonoid benzene ring of the naphthalene nucleus form bluish-green to greenish-yellow solutions in alcohol, except 3-amino-12-phenylis-naphthaphenazonium 12-chloride, $NH_2 \cdot C_{10}H_5 \begin{smallmatrix} \text{N} \\ \text{NPhCl} \end{smallmatrix} > C_6H_4$, which gives a violet solution.

Isomerides of rosinduline in which the amino-group is contained in the benzene ring attached to the quaternary nitrogen atom (in position 7) have been prepared as follows. By condensing *o-p*-diaminodiphenylamine with 4-amino- β -naphthaquinone, a product containing an amino-group in the naphthalene ring in the para-position to the tertiary nitrogen atom is obtained, and by the action of acetic anhydride on this compound in the cold only the amino-group of the benzene ring is attacked. After removing the amino-group in the naphthalene ring by diazotisation, &c., and then hydrolysing the acetyl derivative, 7-*p*-aminophenyl-naphthaphenazonium 7-chloride, $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{N}(C_6H_4 \cdot NH_2)Cl \end{smallmatrix} > C_6H_4$, is obtained. This compound and the corresponding meta-derivative have practically the same colour as phenyl-naphthaphenazonium itself, hence the introduction of the amino-group, in this case as in the similar case of the phenosafranines (*Ber.*, 1895, 27, 3318), does not affect the colour. A complete table of the absorption spectra of the isomerides of rosinduline is given in the original paper. E. W. W.

Triazan Derivatives. By HUGO VOSWINCKEL (*Ber.*, 1899, 33, 2793—2798. Compare *Abstr.*, 1899, i, 958).—The *silver* compound, $C_8H_8ON_3Ag$, of hydroxyphenylethenylcyclotriazan is decomposed on crystallisation from aqueous ammonia, alcohol, or ether, but dissolves in benzene and can be precipitated from this solution by light petroleum.

Methoxyphenylethenylcyclotriazan, $NPh \begin{smallmatrix} \text{N(OMe)} \\ \text{N} \end{smallmatrix} > CMe$, obtained from the foregoing silver compound by means of methyl iodide, is a red-dish oil which solidifies in a mixture of solid carbon dioxide and ether, melts below 0° , boils at 135° under 14 mm. pressure, is insoluble in water, but dissolves in alcohol, ether, or benzene, and with concentrated sulphuric acid gives the same intense coloration as the parent substance.

Phenylmethylcyclomethylenetriazan is obtained by reducing the foregoing methyl ether with a cold alcoholic solution of stannous chloride. The *hydrogen oxalate*, $C_8H_{11}N_3C_2O_4H_2$, forms a transparent, granular powder, and, after drying at 105° , melts at 200° .

Carbanilphenylethylideneoxycyclotriazan, $N \begin{smallmatrix} \text{NPh} \cdot \text{N(CO} \cdot \text{NHPh)} \\ \text{N} \end{smallmatrix} > O$, prepared from the hydroxytriazan and phenylcarbimide, crystallises in

slender, orange needles melting at 127° , is insoluble in water and dilute alkali, but dissolves readily in benzene or hot absolute alcohol. From the latter medium, it separates on addition of water.

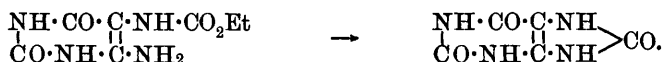
Acetylphenylethylideneoxycyclotriazan, $\begin{array}{c} \text{NPh} \cdot \text{N}^{\text{Ac}} \\ \text{N} = \text{CMe} \end{array} \text{O}$, crystallises from dilute alcohol in beautiful, lustrous, golden needles melting at 103° , is soluble in alcohol, ether, or benzene, but insoluble in water, and is hydrolysed by cold, dilute alkalis or ammonia. *Picrylphenylethylideneoxycyclotriazan*, $\begin{array}{c} \text{NPh} \cdot \text{N}(\text{C}_6\text{H}_2\text{O}_6\text{N}_3) \\ \text{N} = \text{CMe} \end{array} \text{O}$, forms small, shining, orange needles which explode at 140° , is insoluble in alcohol and light petroleum, but is readily soluble in benzene. A. L.

Synthesis of Uric Acid, Xanthine. Theobromine, Theophylline, and Caffeine from Cyanoacetic Acid. By WILHELM TRAUBE (*Ber.*, 1900, **33**, 3035—3056. Compare Abstr., 1900, i, 416). —The formyl derivative of 4:5-diamino-2:6-dioxypyrimidine (*loc. cit.*) yields a sodium derivative, and when this is heated at 100 — 220° xanthine is formed:



The reaction of cyanoacetic acid with carbamide in the presence of phosphorus oxychloride is not satisfactory, however; the yield can, indeed, be increased by adding pyridine, but in practice it is still better to convert cyanoacetic acid into xanthine by passing through guanine as an intermediate stage.

Just as 4:5-diamino-2:6-dioxypyrimidine will condense with formic acid, so it condenses with ethyl chloroformate in the presence of sodium hydroxide; the *urethane* formed can be converted into a sodium derivative, and when this is heated at 150 — 190° uric acid is formed:



From carbamide both xanthine and uric acid can thus be prepared by means of cyanoacetic acid, &c. By a similar series of reactions methylcarbamide can be converted successively into *cyanoacetylmethylcarbamide*, 3-methyl-4-amino-2:6-dioxypyrimidine, the *isonitroso*-derivative of the latter, and 3-methyl-4:5-diamino-2:6-dioxypyrimidine. This forms on the one hand a *formyl* derivative, the sodium salt of which yields 4-methylxanthine (Fischer and Ach, Abstr., 1898, i, 700); on the other hand, it condenses with ethyl chloroformate to a *urethane*, and this, when heated to 230 — 240° , forms a 4-methyluric acid which may be either the δ (von Loeben, Abstr., 1898, i, 128) or the ζ acid (Fischer and Ach, Abstr., 1900, i, 63).

In like fashion, symmetrical dimethylcarbamide can be converted successively into 1:3-dimethyl-4-amino-2:6-dioxypyrimidine (the cyanoacetyldimethylcarbamide, which is presumably formed at first, undergoes an immediate conversion into the pyrimidine), its *isonitroso*-

derivative, and 1:3-dimethyl-4:5-diamino-2:6-dioxypyrimidine. This yields a *formyl* derivative which melts at 252° and is converted into 4:6-dimethylxanthine (theophylline); it reacts with methyl iodide and alcoholic sodium ethoxide, forming 1:4:6-trimethylxanthine (caffeine); it condenses with ethyl chloroformate to a *urethane*, which melts at 206—207° and is converted into 4:6-dimethyluric acid (Fischer and Ach, Abstr., 1896, i, 12); and it reacts with sodium nitrite in hydrochloric acid solution forming an *azimide*,

$$\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \\ | \quad \quad | \\ \text{CO} \cdot \text{NMe} \cdot \text{C} - \text{N} \gg \text{N} \end{array}$$

C. F. B.

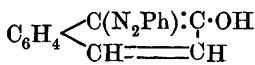
Action of Methylene-Chlorohydrin on Aromatic Amines. By GIUSEPPE GRASSI-CRISTALDI and F. SCHIAVO-LENI (*Gazzetta*, 1900, 30, ii, 112—122).—On mixing cold benzene solutions of aniline- and methylene-chlorohydrin, the hydrochloride of a reddish, oily base, $\text{C}_{28}\text{H}_{28}\text{N}_4$ (or $\text{C}_{14}\text{H}_{14}\text{N}_2$), is obtained. The base is slightly soluble in light petroleum, benzene, carbon disulphide, carbon tetrachloride, ether, or methyl or ethyl alcohol, and readily so in chloroform; it dissolves also in dilute sulphuric, hydrochloric, or acetic acid, yielding a red solution. The *hydrochloride* is white, but gradually becomes yellow and finally coral-red. The yellow *platinichloride*, $\text{C}_{28}\text{H}_{28}\text{N}_4 \cdot \text{H}_2\text{PtCl}_6$, loses 2HCl at 110°, giving the pale green compound, $\text{C}_{28}\text{H}_{28}\text{N}_4 \cdot \text{PtCl}_4$, whilst if the platinichloride is treated with boiling water until the latter has no longer an acid reaction, 4HCl are eliminated and a dark-green product, $\text{C}_{28}\text{H}_{26}\text{N}_4 \cdot \text{PtCl}_2$, remains.

The homologous base, $\text{C}_{32}\text{H}_{36}\text{N}_4$ (or $\text{C}_{16}\text{H}_{18}\text{N}_2$), obtained from *o*-toluidine and methylene-chlorohydrin, is oily, and dissolves slightly in alcohol or ether and readily in chloroform; it also gives red solutions with dilute acids. The *platinichloride* is an amorphous, yellow powder which loses 2HCl and becomes pale green at 110°, whilst when treated with boiling water, 4HCl are evolved and a dark green product, $\text{C}_{32}\text{H}_{34}\text{N}_4 \cdot \text{PtCl}_2$, remains.

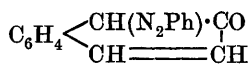
T. H. P.

Unstable Isomerides of the Azo-derivatives of β -Naphthol. By MARIO BETTI [with GIOVANNI LEONCINI] (*Gazzetta*, 1900, 30, ii, 164—177).—When prepared by the action of diazobenzene hydrochloride on a sodium hydroxide solution of β -naphthol and crystallised from alcohol, benzeneazo- β -naphthol is obtained in red needles with a green, metallic lustre melting at 133°; in benzene solution, it gives an intense violet coloration with ethereal ferric chloride, and hence appears to have an enolic structure. On boiling this compound with a 50 per cent. potassium hydroxide solution, it is converted into a black, crystalline mass which exhibits a contraction at 136°, melts at 180—185°, and when kept changes into microscopic, red needles having an indefinite melting point between 130° and 175°. The black crystals melting at 180—185° are completely soluble in alcohol, benzene, chloroform, acetone, acetic acid, or ethyl acetate, any of these solutions yielding, either by crystallisation, evaporation, or precipitation with water or light petroleum, red needles of an *isomeride* melting at 137°; the latter is also obtained, together with a black residue of the same composition melting at 185—187°, when the black

crystals are recrystallised from light petroleum. The two modifications of benzenazo- β -naphthol thus obtained, melting at 133° and 137° respectively, yield the same nitro-derivative melting at 195° , but when brominated in acetic acid solution, the former gives a *heptabromo*-derivative, $C_{16}H_5ON_2Br_7$, separating from benzene in reddish-brown crystals with a metallic lustre and melting at 210 — 215° whilst the form melting at 137° gives rise to a *pentabromo*-compound, $C_{16}H_7ON_2Br_5$, crystallising from benzene as a lustrous red substance melting at about 250° . The following constitutions are ascribed to the two benzenazo- β -naphthols:



Melting point 137° .



Melting point 133° .

o-Tolueneazo- β -naphthol, melting at 132° , when boiled with 50 per cent. aqueous potassium hydroxide, is converted into a black mass having a very marked green metallic lustre and melting at 115° . When kept, the colour of this substance rapidly changes to red, the melting point at the same time rising to 120 — 122° ; by treatment with light petroleum, a black, insoluble mass melting at 120° is then separated from the red form which is found to be the original compound melting at 132° .

In a similar manner, *p*-tolueneazo- β -naphthol yields a brown modification which when heated in a melting point tube becomes lighter in colour and melts at the same temperature as the original compound.

T. H. P.

Condensation of Benzhydrols with *p*-Hydroxyazo-compounds and the Structure of the Latter. By RICHARD MÖHLAU and ERNST KEGEL (*Ber.*, 1900, 33, 2858—2873).—The *phenylhydrazones*, $\text{NHPh} \cdot \text{N} : \text{C}_{10}\text{H}_5\text{O} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, of α -naphthaquinonetetramethyldiaminodiphenylmethane (Abstr., 1899, i, 912) is identical with the compound obtained from the condensation of benzenazo- α -naphthol with "Michler's hydrol," $\text{OH} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, in absolute alcohol; from the latter it separates in bright-red needles with a metallic lustre, melts at 200.5° , and is insoluble in aqueous alkalis. The *hydrochloride*, $\text{C}_{33}\text{H}_{32}\text{ON}_4 \cdot 3\text{HCl}$, and the *picrate*, $\text{C}_{33}\text{H}_{32}\text{ON}_4 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, form red needles, the latter melting and decomposing at 201° . The *acetyl* derivative crystallises in dark yellow, microscopic prisms, decomposes at 123° , and on reduction with zinc dust and acetic acid yields exclusively acetanilide and 1-amino-4-naphthol-2-tetramethyldiaminodiphenylmethane, $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{NH}_2) \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, which crystallises from ethyl acetate in colourless prisms, melts at 109 — 110° , and condenses with diazo-compounds in alkaline, but not in acid solutions; with warm hydrochloric acid it yields 1 : 4-naphthaquinol-2-tetramethyldiaminodiphenylmethane, $\text{C}_{10}\text{H}_5(\text{OH})_2 \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, which is readily oxidised by the air to the corresponding α -quinone, and yields a crystalline *hydrochloride*, $\text{C}_{27}\text{H}_{28}\text{O}_2\text{N}_2 \cdot 2\text{HCl}$.

Benzhydrol does not interact with benzenazo- α -naphthol in alcoholic solution, but when dissolved in glacial acetic acid they yield the compound $\text{NHPh} \cdot \text{N} : \text{C}_{10}\text{H}_5\text{O} \cdot \text{CHPh}_2$, which crystallises from benzene, on

adding light petroleum, in microscopic, yellow plates, melts at 246—250°, and is insoluble in aqueous alkalis.

Diphenyldisazo- α -naphthol, $C_{12}H_8(\cdot N_2 \cdot C_{10}H_6 \cdot OH)_2$ or $C_{12}H_8(NH \cdot N : C_{10}H_6 \cdot O)_2$,

obtained by combining α -naphthol with diazotised benzidine, crystallises from pyridine in prisms with a greenish lustre, softens at 200°, and melts at 209—210°; with Michler's hydrol, it yields the compound, $C_{12}H_8[NH \cdot N : C_{10}H_5O \cdot CH(C_6H_4 \cdot NMe_2)_2]_2$, which crystallises from pyridine in bluish-violet, concentrically-grouped needles, sinters at 150° and melts at 164—165°; on reduction with zinc dust and warm hydrochloric acid, it yields benzidine and α -naphthaquinoltetramethyldiaminodiphenylmethane.

Dianisylidisazo- α -naphthol, $C_{34}H_{26}O_4N_4$, is a brownish, crystalline powder with a greenish lustre, which softens at 210°, melts at 218—219°, and dissolves in aqueous alkalis; with Michler's hydrol, it yields the compound, $C_{68}H_{66}O_4N_8$, which softens at 165°, melts at 180°, and could not be obtained crystalline.

Benzoquinonephenylhydrazonetetramethyldiaminodiphenylmethane,

$NHPh \cdot N : C_6H_3O \cdot CH(C_6H_4 \cdot NMe_2)_2$,

from Michler's hydrol and *p*-hydroxyazobenzene dissolved in boiling absolute alcohol, crystallises from ethyl acetate in well-formed, yellow prisms and melts at 218°. No action occurs when *p*-methoxyazobenzene is boiled with Michler's hydrol for several days in absolute alcohol solution, and with benzeneazo- β -naphthol the same is true.

From the foregoing facts, the authors conclude that *p*-hydroxyazo-compounds in the free state are probably quinonehydrazones (compare McPherson, *Abstr.*, 1900, 123; Hantzsch and Farmer, *ibid.*, 122 Auwers, *ibid.*, 418).

W. A. D.

Tetrazones. By ANGELO ANGELI (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 180—183).—Nitrohydroxylaminic acid acts on piperidine with formation of products varying with the conditions of the reaction. Those which have been separated are: (1) the nitrosoamine, $C_5NH_{10} \cdot NO$; (2) a yellow oil with a nauseating odour recalling that of phosphorus and of its pentachloride; this is probably the oxyazo-compound, $ON_2(C_5NH_{10})_2$; (3) the tetrazone, $N_2(C_5NH_{10})_2$.

T. H. P.

Proteids. By JOSEF HABERMANN and R. EHRENFELD (*Zeit. physiol. Chem.*, 1900, 30, 453—472).—A critical and experimental examination of Schützenberger's results and theories concerning the decomposition products and constitution of proteids.

W. D. H.

Nucleo-histon. By IVAR BANG (*Zeit. physiol. Chem.*, 1900, 30, 508—519. By ALBRECHT KOSSEL (*ibid.*, 520—522).—According to the first paper, Lilienfeld's nucleo-histon is a nucleo-proteid, and it neither contains, nor yields, histon. The second paper is a criticism on the first; Lilienfeld's work is regarded as still trustworthy, the investigation published in the first paper having confused the issue whether there is such a thing as nucleo-histon with the question whether or no it is preformed in the cells.

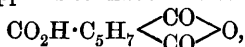
W. D. H.

Antipeptone. By MAX SIEGFRIED (*Ber.*, 1900, 33, 2851—2858. Compare *Abstr.*, 1895, i, 76; 1898, i, 611; 1899, i, 179).—Kuhne's method

for the isolation of antipeptone does not give a pure product, since saturation with ammonium sulphate in neutral, alkaline, or acid solution does not precipitate the last traces of albumoses and since antipeptone itself when evaporated on the water-bath yields small amounts of albumoses. To completely precipitate the albumoses, it is necessary to use large quantities of sulphuric acid in addition to saturated ammonium sulphate, and then to precipitate with potassium iron alum; the solution obtained by decomposing the iron precipitate can readily be freed from albumoses by stirring with saturated ammonium sulphate.

Two acids, $C_{10}H_{17}O_5N_3$ and $C_{11}H_{19}O_5N_3$ have been isolated from antipeptone and their *zinc* and *barium* salts prepared. Neither acid appears to be identical with carnic acid, for which the formula $C_{10}H_{15}O_5N_3$ has been previously suggested J. J. S.

Constitution of the Hæmatic Acids. By WILLIAM KÜSTER (*Ber.*, 1900, 33, 3021—3025. Compare *Abstr.*, 1899, i, 468).—The "anhydride of tribasic hæmatic acid," although it takes up 2 mols. of ammonia or aniline, appears to have the constitution



for it yields no acetyl or benzoyl derivative, and a *trimethyl ester*, $C_5H_7(CO_2Me)_3$, boiling at 300° can be obtained from it, in addition to a trisilver salt. Among the saturated tribasic acids, $C_8H_{12}O_6$, obtained by reducing it with hydriodic acid, is one that resembles Auwer's ethyltricarballic acid. By elimination of carbon dioxide, it yields the anhydride of a dibasic acid, $C_5H_8(CO_2H)_2$.

"Dibasic hæmatic acid" must then be regarded as the imide of the tribasic acid $CO_2H \cdot C_5H_7 \begin{array}{c} \diagup CO \diagdown \\ \diagdown CO \diagup \end{array} NH$. In harmony with this view is the fact that its disilver derivative forms a methyl ester, when treated with methyl iodide, from which methylamine is obtained by hydrolysis. Moreover, it is formed from the anhydride of the tribasic acid by heating this with alcoholic ammonia at 110° ; at a somewhat higher temperature, carbon dioxide is eliminated, and a substance is obtained which has all the properties of an *imide* of the maleic series, $C_5H_8 \begin{array}{c} \diagup CO \diagdown \\ \diagdown CO \diagup \end{array} NH$; it melts at $72-73^\circ$. This yields two barium salts when hydrolysed with barium hydroxide. One crystallises in plates; acids react with this and form the *anhydride*, $C_5H_8 \begin{array}{c} \diagup CO \diagdown \\ \diagdown CO \diagup \end{array} O$, which boils at $228-229^\circ$, and dissolves in alkalis; the *silver*, *barium*, and *calcium* salts were prepared. The second of the two barium salts crystallises in needles; the *acid* from which it is derived, $C_7H_{10}O_4$, is crystalline, and melts and decomposes at 175° ; it is, perhaps, a homologue of itaconic acid; its *calcium* salt, $C_7H_8O_4Ca \cdot H_2O$, crystallises in needles. C. F. B.

Protease of *Aspergillus Niger*. By G. MALFITANO (*Ann. Inst. Pasteur*, 1900, 14, 420—448. Compare *ibid.*, 60).—The protease of *Aspergillus niger* resembles proteolytic diastases, and is very similar to papaine and the proteolytic diastase of malt. It acts on gelatin, on the nucleo-albumins, the globulins and albuminates, but not on egg-albumin.

As regards reaction, the most favourable is neutrality to methyl-orange, that is, the acidity of acid phosphates.

Protease differs from papaine only in being more sensitive to the injurious action of alkaline phosphates; it is very distinct from pancreatine, which is active in presence of alkaline phosphates.

N. H. J. M.

An Oxydase in Valerian. By P. CARLES (*J. Pharm.*, 1900, [vi], 12, 148—150).—The fact that valerian only acquires its odour on keeping, and that the freshly cut root gives an intensely blue coloration with tincture of guaiacum, suggests the presence of an oxydase in the plant; on bruising the root with a little water and adding alcohol, white flakes are precipitated which are extremely sensitive to the tests for oxydases. The oxydase is destroyed in the roots by heating them either alone or with water at 100°; like other oxydases, that of valerian appears to contain manganese, since this is present in quantity in the ash of the root.

W. A. D.

Endotrypsin, an Enzyme from Yeast. By MARTIN HAHN and LUDWIG GERET (*Zeit. Biol.*, 1900, 40, 117—172).—The name *endotrypsin* is applied to an enzyme which is found in the liquid from crushed yeast cells, and which acts, not only on the proteids in the juice, but on other proteids as well. It is probably preceded in the cell-protoplasm by a zymogen, the transformation of which into enzyme occurs in accordance with the needs of the organism for intracellular katabolic processes. The enzyme is not dialysable; it is precipitated by most reagents that precipitate proteids, but does not give Millon's or the biuret reaction. The optimum temperature for its reaction is 40—45°; it continues acting at 37° for 15 days. It is destroyed at 60°. The enzyme appears to be a new type; it resembles pepsin in requiring the presence of an acid, and trypsin in the nature of its products. After digestion, leucine, tyrosine, and other amino-acids are found in abundance; proteoses are found in small quantity. Peptone as an intermediate product was not detected.

W. D. H.

Expressed Yeast-Cell Plasma (Buchner's "Zymase"). By ALLAN MACFADYEN, GEORGE HARRIS MORRIS, and SIDNEY ROWLAND (*Ber.*, 1900, 33, 2764—2790; *Proc. Roy. Soc.*, 1900, 67, 250—266).—A large number of experiments have been carried out by the authors on the extracts of various top-fermentation yeasts under conditions similar to those of Buchner's researches with bottom-fermentation yeasts. An improved method of treating the yeast has been devised which allows of quicker working than before. The yeast is well washed and then freed from water by enclosing it in a double thickness of hydraulic-press cloth and submitting it to a pressure of 70—100 atmospheres. The white powder thus obtained is mixed with sand and pounded in a specially designed apparatus, the temperature not being allowed to rise above 15°. Kieselguhr is then added and the extracted liquid separated by subjecting the mass to a pressure of 250—300 atmospheres. The resulting extract, which shows very wide variations in fermenting power

probably differs less in composition from the ferment actually present in the living yeast cells than does that prepared by Buchner's method, in which water is mixed with the pounded yeast. The yield and also the activity of the extract is in general greatest from yeasts which have been removed from the fermenting vessels two or three days before treatment. The extract undergoes considerable fermentation on keeping, even at temperatures so low as to solidify it, and in nearly every case, the evolution of carbon dioxide was greater than when sugar was present. The action on sugar is increased by rise of temperature and of the various sugars sucrose gives the greatest volume of gas. Dilution of the extract with an equal volume of water diminishes its activity, whilst if two volumes of water be added the evolution of gas is considerably decreased. Marked diminution in activity accompanied by a decrease in the specific gravity is also produced by passing the extract through a Chamberland or Berkefeld filter. In the case of very active extracts, the ratio of the amounts of alcohol and carbon dioxide formed by their action on sugar is approximately the same as in ordinary fermentation by yeast, but with those less active there seems to be no definite relation existing between the proportions of these products. At the same time, the quantity of sugar destroyed is far greater than corresponds with the amounts of alcohol and carbon dioxide formed during fermentation.

To explain their results, which are not in accord with Buchner's enzyme theory of the fermenting action of yeast extract, the authors suppose that the fermentation of sugar solutions by yeast takes place in two stages (1) incorporation of the sugar molecule with the living yeast (anabolism); (2) decomposition of the complicated material thus formed into simpler products, generally carbon dioxide and alcohol (katabolism). These assumptions made, the auto-fermentation of the yeast extract is explained as due to the presence in it of a protoplasm-sugar compound, which undergoes gradual decomposition with formation of carbon dioxide and alcohol; in the case of an active extract, this decomposition proceeds nearly to completion, whilst with one less powerful, the activity of the protoplasmic constituent causing the fermentation ceases, while an excess of sugar still remains in the solution in combination with it.

T. H. P.

Organic Chemistry.

Analogies between Oxygen, Nitrogen, and Carbon in similar Linkings. By EMIL ERLENMEYER, jun. (*J. pr. Chem.*, 1900, [ii], 62, 145—165).—A paper which summarises the results of introducing different atomic groupings into analogous compounds, but does not lend itself to abstraction. R. H. P.

Action of Bromine on 1:1-Dimethyltrimethylene. By GABRIEL GUSTAVSON (*J. pr. Chem.*, 1900, [ii], 62, 270—272).—The bromine compound previously described (Gustavson and Popper, *Abstr.*, 1899, i, 263), and obtained by the action of bromine on 1:1-dimethyltrimethylene (1:1-dimethylcyclopropane), is $\beta\gamma$ -dibromoisobutane, $\text{CMe}_2\text{Br}\cdot\text{CHMeBr}$. R. H. P.

Derivatives of cyclopentadiene. By FRITZ NOELDECHEN (*Ber.*, 1900, 33, 3348—3354).—The chlorocyclopentene obtained by the addition of hydrogen chloride to Kraemer and Spilker's cyclopentadiene (*Abstr.*, 1896, i, 289) interacts with aniline below 10° to form anilinocyclopentene, $\text{C}_5\text{H}_7\cdot\text{NHPh}$, a colourless oil boiling at 152 — 153° under 25 mm., and at 260° under the ordinary pressure; the hydrochloride crystallises from absolute alcohol in short prisms, and melts and decomposes at 140 — 142° ; the platinichloride (with $1\frac{1}{2}\text{H}_2\text{O}$) decomposes at 140° ; the picrate melts and decomposes at 154 — 155° , the sparingly soluble sulphate at 197° , and the oxalate at 122° . The acetyl derivative, $\text{C}_5\text{H}_7\cdot\text{NAcPh}$, crystallises from water in long needles, and melts at 128° ; the benzoyl derivative separates in transparent, hexagonal prisms from light petroleum and melts at 76 — 77° .

cyclopentenyl diphenylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{NPh}\cdot\text{C}_5\text{H}_7$, obtained by the action of phenylcarbimide on the base at the ordinary temperature, separates from absolute alcohol in small leaflets and melts at 112° ; the analogous thiocarbamide crystallises from absolute alcohol in lustrous, colourless needles and melts at 130° .

Anilinocyclopentene interacts with nitrous acid to form a reddish-yellow, oily nitrosoamine, which shows Liebermann's reaction, and is reduced by zinc dust and acetic acid to cyclopentenylphenylhydrazine, $\text{NH}_2\cdot\text{NPh}\cdot\text{C}_5\text{H}_7$, the hydrochloride of which forms silvery scales and melts and decomposes at 215 — 217° .

On heating anilinocyclopentene with hydriodic acid, or with concentrated hydrochloric acid for 2 hours at 200° , aniline is formed, together with a red, amorphous, insoluble substance. On attempting to reduce the base with sodium and amyl alcohol, an isomeric anilinocyclopentene is formed, instead of the expected anilinocyclopentane; its hydrochloride is more sparingly soluble than that of the original base, and forms long, white needles melting and decomposing at 168° ; the platinichloride (with $2\text{H}_2\text{O}$) decomposes at 135° .

Piperidylcyclopentene, $\text{C}_5\text{H}_{10}\text{N}\cdot\text{C}_5\text{H}_7$, from chlorocyclopentene and piperidine at -5° , boils at 94 — 96° under 23 mm., and at 206 — 207°

under the ordinary pressure ; it absorbs carbon dioxide from the air, yields a crystalline *methiodide*, and a hygroscopic *hydrochloride* and *sulphate*, the former decomposing at 190° . W. A. D.

Abnormal Behaviour of Polyhaloid Compounds with Alcoholic Potash. By IWAN L. KONDAKOFF (*J. pr. Chem.*, 1900, [ii], 62, 166—188. Compare Abstr., 1899, i, 556).—The previous work (*loc. cit.*) has been repeated, and it is now shown that the action of alcoholic potash on $\beta\gamma$ -dimethyl- β -butylene dibromide produces diisopropenyl, $\beta\gamma$ -dimethyl- β -butylene, and an unsaturated *ether*, which boils at 136 — 146° , and, when treated with dilute sulphuric acid, gives pinacone, pinacolin, and an aldehyde. $\beta\gamma$ -Dimethyl- β -butylene dichloride, when treated with alcoholic potash, yields diisopropenyl and the ether boiling at 136 — 146° .

Diisopropenyl forms two *dibromides*, the one is an oil, and the other crystallises in colourless needles, which have an irritating odour and melt at 47° , both yield the same *tetrabromide* melting at 137° . The crystalline dibromide, when oxidised, yields two glycols, of which one has the composition $C_6H_{12}O_2Br_2$, crystallises in prisms, and melts at 94° ; the other, obtained in very small quantity, melts at 160° .

The paper contains a discussion of the constitution of bromides formed by unsaturated hydrocarbons from the point of view of Thiele's theory of "partial" valencies (Abstr., 1899, i, 554).

R. H. P.

Diethyl Peroxide. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1900, 33, 3387—3393).—Diethyl sulphate was shaken with hydrogen peroxide of 12 per cent. strength (by weight), 50 per cent. aqueous potassium hydroxide being added little by little ; the temperature was not allowed to rise above 20° , and the operation was continued (for some 11 hours) until the presence of hydrogen peroxide could be detected no longer. The product was then made acid with sulphuric acid and fractionated ; the fraction coming over at 55 — 75° consisted mainly of diethyl peroxide, that distilling at 75 — 100° probably contained some ethyl hydrogen peroxide. *Diethyl peroxide*, O_2Et_2 , boils at 65° , and has a sp. gr. 0.8273 at $15^{\circ}/4^{\circ}$; it is strikingly inert in its reactions, almost resembling an ether ; permanganate, chromic acid, and sodium amalgam do not affect it, and it oxidises alkaline pyrogallol and potassium iodide but slowly ; it is, however, reduced quantitatively to ethyl alcohol by zinc in the presence of acetic and dilute sulphuric or hydrochloric acid ; the "active" oxygen in it may be determined in this way by taking a weighed quantity of zinc and measuring the deficit in the hydrogen evolved as compared with that equivalent to the amount of zinc taken. The inflammability of the vapour is most striking ; it inflames in air at 250° , or 50° below the kindling temperature of carbon disulphide vapour, and when a hot copper wire is brought near it in an atmosphere of carbon dioxide, the liquid disappears rapidly, without any noise, without any flash, and without boiling. As a result of this internal combustion, formaldehyde, carbon monoxide, and ethane are formed. A mixture of the vapour with air or oxygen explodes more violently than a mixture of hydrogen with air or oxygen. On the other hand, the liquid

could not be made to explode by hammering, or by the use of mercury fulminate.

The ready reduction of diethyl peroxide to ethyl alcohol is regarded as strong evidence in favour of the formula $\text{HO}\cdot\text{OH}$, rather than $\text{O}:\text{OH}_2$, for hydrogen peroxide. C. F. B.

Optically Active Forms of α -Bromopropionic Acid. By LUDWIG RAMBERG (*Ber.*, 1900, **33**, 3354—3356).—On adding cinchonine gradually to an aqueous solution of α -bromopropionic acid, thick prisms or plates of the salt, $\text{C}_{19}\text{H}_{22}\text{ON}_2\cdot 2(\text{C}_3\text{H}_5\text{O}_2\text{Br})$, of the *l*-acid separate; the pure acid appears to have $[\alpha]_D -7.55^\circ$ at 24° , the *d*-acid, isolated from the mother liquors of the foregoing salt, having $[\alpha]_D +7.44^\circ$. These values, however, are to be more accurately determined. W. A. D.

$\delta\epsilon$ -Hexenoic Acid. By FRITZ FICHTER and WERNER LANGGUTH (*Annalen*, 1900, **313**, 371—381. Compare Wallach, *Abstr.*, 1900, i, 589).—The paper contains experimental details relating to the preparation of $\delta\epsilon$ -hexenoic acid (*Abstr.*, 1897, i, 590), and of $\gamma\delta$ -hexenoic acid (*Abstr.*, 1897, i, 14). M. O. F.

Action of Water on Heptylamine Soaps. By FRIEDRICH KRAFFT and R. FUNCKE (*Ber.*, 1900, **33**, 3210—3212).—When heptylamine oleate (m. p. 14°), elaidate (m. p. 45°), erucate (m. p. 21.5°), or brassate (m. p. 44.5°) is brought into contact with water at a temperature above the melting point, globular or thread-like bodies are produced, which grow in size when surrounded with water, but collapse in contact with a strong salt solution, the surface of the globules acting as a semi-permeable membrane. By cooling below the melting point, the globules disappear and crystals are again formed; within certain limits of temperature, globules and crystals may both be observed. T. M. L.

Transformation of Maleic Acid into Fumaric Acid. By JULIUS SCHMIDT (*Ber.*, 1900, **33**, 3241—3243. Compare Wislicenus, *Verhand. K. Ges. Wiss. Leipzig*, 1895, 489).—Maleic acid, dissolved in dry ether, is not affected by the nitrous fumes evolved from a mixture of arsenious oxide and nitric acid; an aqueous solution, cooled below 10° , when similarly treated, yields a mixture of unaltered substance and fumaric acid, whilst at the temperature of the water-bath 70° per cent. of the maleic acid is transformed. Fumaric acid is not produced when an aqueous solution of its *cis*-isomeride is heated on the water-bath, and no alteration results from the addition of nitric acid free from nitrous acid (compare Edmed, *Proc.*, 1899, **15**, 190). G. T. M.

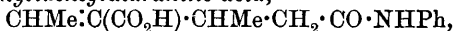
Dicrotonic Acid. By HANS VON PECHMANN (*Ber.*, 1900, **33**, 3323—3341).—*Dimethyl dicrotonate* (dimethyl β -methyl- α -ethylidene-glutarate), formed by the action of sodium methiodide on dimethyl crotonate, is a colourless oil boiling at 120° under 15 mm. and at 130° under 20 mm. pressure; it is also formed when dicrotonic acid is treated with diazomethane. *Diethyl dicrotonate* is prepared from diethyl crotonate, and boils at 137.5° under 18 mm. pressure. *Dicrotonic acid*, $\text{CHMe}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared from the ester by hydrolysis, crystallises in white, compact needles melting at 129° , and boils

at 210° under 21 mm. pressure, partial decomposition into water and anhydride taking place. The acid is dibasic to soda, and has a conductivity K 0 00281. The difference of equivalent conductivity of the sodium salt at dilutions of 32 litres and 1024 litres is 11·9, an abnormally low value for a dibasic acid. The *barium* salt crystallises with $1\text{H}_2\text{O}$ in lustrous scales; no acid salts could be obtained. *Monomethyl dicrotonate*, $\text{CHMe}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is obtained by the action of alcoholic sodium ethoxide on dicrotonic anhydride, and is an oil boiling at 174° under 16 mm., at 186° under 34 mm., and at 192° under 44 mm. pressure. *Dicrotonic anhydride*, $\text{CHMe}\cdot\text{C}\begin{matrix} \diagup \text{CHMe}\cdot\text{CH}_2 \\ \diagdown \text{CO}-\text{O}-\text{CO} \end{matrix}$,

formed when the acid is distilled under atmospheric pressure or treated with acetyl chloride, crystallises in white needles melting at 38—39° and boiling at about 300°.

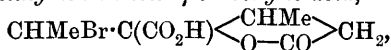
The constitution of the acid is shown by the fact that on oxidation with potassium permanganate it yields acetaldehyde and methylsuccinic acid.

β -Methyl- α -ethylideneglutaranilic acid,



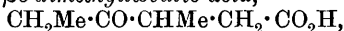
is obtained by the action of aniline on the anhydride, and crystallises in lustrous prisms melting at 178—179°.

Dicrotonic acid readily combines with bromine to form an unstable *dibromide*, which loses hydrogen bromide when heated with water and forms *δ -bromo- β -methylhexolactone- γ -carboxylic acid*,

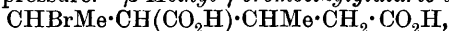


which crystallises in colourless prisms melting at 140°. When its solution in sodium carbonate is boiled, hydrogen bromide and carbon dioxide are eliminated with formation of *β -methylhexenolactone*,

$\text{MeCH}\cdot\text{C}\begin{matrix} \diagup \text{CHMe}\cdot\text{CH}_2 \\ \diagdown \text{O}-\text{CO} \end{matrix}$, which is a colourless oil boiling at 247°. The corresponding acid, *$\beta\delta$ -dimethylævulic acid*,



is a thick oil boiling at 153—154° under 20—21 mm. pressure. The *phenylhydrazone* is a thick oil, whilst the *semicarbazone*, $\text{C}_7\text{H}_{12}\text{O}_2\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is a characteristic, white, crystalline powder melting at 152°. When heated, it yields a pyridazinone, probably a homologue of the 3-methylpyridazinone, which is formed in a similar manner from the semicarbazone of lævulic acid. *$\beta\delta$ -Dimethylævulic acid* can be prepared synthetically from acetonedicarboxylic acid, and its formation in this way affords further confirmation of the constitution of dicrotonic acid. Ethyl dimethylacetonedicarboxylate reacts with ethyl bromoacetate to form *triethyl α_1 -dimethylacetonedicarboxylate*, $\text{CO}_2\text{Et}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CMe}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which boils at 191·5° under 16 mm. pressure. *β -Methyl- γ -bromoethylglutaric acid*,



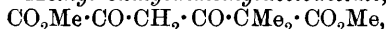
is formed by the combination of hydrogen bromide with dicrotonic acid and crystallises in aggregates of needles; the acid readily loses bromine, and could not be obtained quite pure. When distilled, it forms crotonic acid together with a smaller amount of *β -methyl- $\gamma\delta$ -hex-*

enoic acid, $\text{CHMe}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which is also formed when the acid is heated with water. It is a colourless liquid with a rancid smell, and boils at $209-210^\circ$. With bromine, it forms $\gamma\delta$ -*dibromo- β -methylhexoic acid*, $\text{CHBrMe}\cdot\text{CHBr}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises in rhombic tablets and melts at $135-136^\circ$. β -*Methyl- α -ethylglutaric acid*, $\text{CO}_2\text{H}\cdot\text{CHEt}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is formed by the reduction of β -methyl- γ -bromoethylglutaric acid and crystallises in colourless prisms melting at $100-101^\circ$; $K=0.0067$. A. H.

The β -Lactone of *as*-Dimethylmalic Acid. By FRITZ FICHTER and SYLVAIN HIRSCH (*Ber.*, 1900, 33, 3270—3276).—Bromo-*as*-dimethylsuccinic acid, which could not be obtained pure by von Baeyer and Villiger (*Abstr.*, 1897, i, 597), yields on distillation the pure *anhydride*, $\begin{matrix} \text{CMe}_2\text{---CO} \\ | \\ \text{CHBr}\cdot\text{CO} \end{matrix} \text{>O}$, which forms stout needles, melts at 45° , and boils at $121-123^\circ$ under 13 mm. pressure. On evaporating its aqueous solution in a vacuum, the pure acid, $\text{C}_6\text{H}_9\text{O}_4\text{Br}$, is obtained as a hard, crystalline crust melting at 153° ; if the anhydride is dissolved in benzene containing water, slender needles of the acid with $\frac{1}{2}\text{C}_6\text{H}_6$ separate, which melt at 133° , and effloresce in the air, the acid thus obtained melting at 143° .

The β -lactone of *as*-dimethylmalic acid distils at $145-150^\circ$ under 13 mm. pressure, being converted into the isomeric *anhydride*, $\begin{matrix} \text{CMe}_2\text{---CO} \\ | \\ \text{OH}\cdot\text{CH}\text{---CO} \end{matrix} \text{>O}$, a colourless oil which is also formed on distilling *as*-dimethylmalic acid under the same conditions, although decomposition occurs at atmospheric pressure. Since the anhydride readily absorbs water from the air to form dimethylmalic acid, it differs essentially from the isomeric lactone which crystallises from water unchanged. W. A. D.

Oxalyldialkylacetoacetic Esters. By MAX CONRAD (*Ber.*, 1900, 33, 3432—3438).—*Methyl oxalyldimethylacetoacetate*,



prepared by the action of sodium on an ethereal solution of methyl oxalate and methyl dimethylacetoacetate and purified by converting into the copper compound, is a pale yellow oil which has a sp. gr. 1.193 at $17^\circ/15^\circ$, boils and partially decomposes at $270-278^\circ$, has a distinct acid reaction, mixes readily with ether, alcohol, or benzene, and gives a cherry-red coloration with alcoholic ferric chloride. The *calcium* derivative, $\text{Ca}(\text{C}_{10}\text{H}_{13}\text{O}_6)_2$, dissolves in ether, softens at 115° , and melts at 125° ; the *cobalt* derivative, $\text{Co}(\text{C}_{10}\text{H}_{13}\text{O}_6)_2$, melts at $98-100^\circ$; the *copper* derivative, $\text{Cu}(\text{C}_{10}\text{H}_{13}\text{O}_6)_2$, melts at $128-130^\circ$; the compound with *ammonia*, $\text{C}_{10}\text{H}_{17}\text{O}_6\text{N}$, forms minute, white needles, and melts at 110° . *Methyl anilino-oxalyldimethylacetoacetate*, $\text{CO}_2\text{Me}\cdot\text{C}(\text{NHPh})\cdot\text{CH}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Me}$, or



crystallises from methyl alcohol in large, well-formed, sulphur-yellow prisms and melts at 81° ; the *monoxime*, $\text{C}_{10}\text{H}_{15}\text{O}_6\text{N}$, crystallises from hot water and melts at 91° . *Oxalyldimethylacetoacetic acid* forms colourless crystals, melts at 180° with evolution of carbon dioxide, and

also loses carbon dioxide in aqueous solution at 70—80°, giving an *isobutyrylpyruvic acid*.

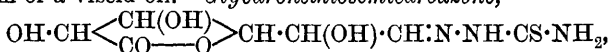
Methyl bromo-oxalyldimethylacetoacetate is a yellow oil; it forms a copper derivative, $\text{Cu}(\text{C}_{10}\text{H}_{12}\text{BrO}_6)_2$, crystallising from ether in green needles. The *thiazyl* derivative, $\text{NH}:\text{C} \begin{smallmatrix} \text{S} \cdot \text{CH} \cdot \text{CO} \cdot \text{CO}_2\text{Me} \\ \text{N} : \text{C} \cdot \text{CM}_2 \cdot \text{CO}_2\text{Me} \end{smallmatrix}$ or

$\text{NH}:\text{C} \begin{smallmatrix} \text{S} \cdot \text{CH} \cdot \text{CO} \cdot \text{CM}_2 \cdot \text{CO}_2\text{Me} \\ \text{N} : \text{C} \cdot \text{CO}_2\text{Me} \end{smallmatrix}$, prepared by the action of thiocarb-

amide on the bromo-ester, crystallises from hot water in white needles and melts at 138°. By the action of potassium acetate on the bromo-ester in methyl alcoholic solution, methyl oxalate and the acetate of methyl hydroxydimethylacetoacetate are produced as decomposition products of methyl acetoxyoxalyldimethylacetoacetate.

Ethyl oxalyldiethylacetoacetate, $\text{CO}_2\text{Et} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CEt}_2 \cdot \text{CO}_2\text{Et}$, is a colourless oil which forms a copper derivative and gives a red coloration with alcoholic ferric chloride. By distillation, it gives *ethyl aa-diethylacetonedicarboxylate*, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CEt}_2 \cdot \text{CO}_2\text{Et}$, boiling at 275—285°. T. M. L.

Glycuronic Acid. I. By CARL NEUBERG (*Ber.*, 1900, 33, 3315—3323).—Several of the compounds described by the author have been previously described by Giemsa (this vol., i, 11). Glycuronolactane (glycurone) is best obtained by boiling euxanthic acid with dilute sulphuric acid. *Glycuroneamylmercaptopal* was only obtained in the form of a viscid oil. *Glycuronethiosemicarbazone*,



crystallises from water in fascicular groups of needles melting at 223°, and is insoluble in the ordinary organic solvents. *Glycurone-diphenylhydrazone*, $\text{C}_6\text{H}_5\text{O}_5 \cdot \text{N}_2\text{Ph}_2$, crystallises in needles melting at 150°. Glycuroneoxime is converted by acetic anhydride and sodium acetate into the tetraacetyl derivative of the seminitrile of *d*-saccharic acid, which has not, however, been obtained pure.

Glycuronic acid forms characteristic salts with many of the alkaloids. The *cinchonine* salt, $\text{C}_6\text{H}_{10}\text{O}_7 \cdot \text{C}_{19}\text{H}_{22}\text{N}_2\text{O}$, crystallises in characteristic white needles melting at 204°, and has $[\alpha]_D + 138.6^\circ$. The *quinine* salt softens at 175°, melts at 180°, and has $[\alpha]_D - 80.1^\circ$. The *brucine* salt crystallises in very slender needles melting at 200°, and the *strychnine* salt closely resembles it.

Glycurone can readily be separated from the sugars by means of its thiosemicarbazone, and glycuronic acid by the aid of the cinchonine salt, whilst the acid is best detected in presence of the sugars by means of the *p*-bromophenylhydrazine compound. A. H.

Acidimetry of Aldehydes and Ketones. By A. ASTRUC and H. MURCO (*Compt. rend.*, 1900, 131, 943—945).—A number of aldehydes and ketones of simple and mixed function were examined as to their behaviour towards the indicators helianthin A, phenolphthalein, and Poirrier's blue.

The simple aliphatic and aromatic aldehydes are neutral towards all three indicators. Glyoxal, the only simple dialdehyde examined, reacts

with one equivalent of alkali, but the process is slow. Halogenated aldehydes, such as chloral hydrate, chloral alcoholate, and bromal, are neutralised by one equivalent of alkali. Hydroxybutyraldehyde and aldehydic sugars are neutral towards all three indicators, whereas salicylaldehyde, *p*-hydroxybenzaldehyde, methylprotocatechuic aldehyde (vanillin), and methyleneprotocatechuic aldehyde (piperonal) are neutral towards helianthin but monobasic towards phenolphthalein or Poirrier's-blue.

The simple aliphatic and aromatic ketones are without action on either of the three indicators. Acetylacetone is exactly monobasic towards Poirrier's-blue, but behaves less definitely with phenolphthalein. The exact titration of methylacetylacetone is impossible with either of these indicators. Acetonylacetone is neutral. Chloroacetone and bromoacetophenone are neutral towards helianthin and monobasic towards phenolphthalein or Poirrier's-blue. The ketonic sugars are neutral. Pyruvic and lævulic acids are exactly monobasic towards phenolphthalein or Poirrier's-blue, but with helianthin the neutral point is reached before one equivalent of alkali has been added.

N. L.

Search for other Sugars than Xylose and Dextrose in the Products of the Hydrolysis of Wood from the Trunks of Trees. By FRANCIS H. STORER (*Bull. Bussey Inst.*, 1900, 2, 437—467).—The author has submitted samples of wood from the trunks of the sugar maple (*Acer saccharinum*) and birch (*Betula populifolia*), and from the root of the former tree to the action of hydrochloric and sulphuric acids under various conditions, and determined the cupric-reducing and rotatory powers of the solutions thus produced, in order to obtain, if possible, indications of the presence in wood of substances hitherto undetected. Cotton cloth was also subjected to the same treatment. The results of these experiments led to the following conclusions.

When strong sulphuric acid is allowed to act on cellulose, and the product boiled with dilute acid, the whole of the cellulose is not readily converted into dextrose, as has been frequently stated.

The compounds which carbohydrates form with sulphuric acid are very difficult to decompose by long continued boiling, and, as a general rule, a considerable part of the organic matter with which the strong acid at first united is not changed into dextrose when subsequently boiled with the dilute acid; some part of this undecomposed substance remains admixed with the dextrose syrup, and tends finally to contaminate the solid dextrose. If the calcium or barium salts of these compounds of carbohydrates with sulphuric acid are boiled for a long time, some quantity of the salts is liable to remain undecomposed and render the dextrose syrup impure; when such syrups are concentrated, crystals of two kinds are obtained, one of which consists entirely of inorganic matter. Béchamp (*Ann. chim. phys.*, 1831, [ii], 48, 502) appears to have mistaken the latter substance for sugar, and it is probably due to the same cause that Berthelot (*Ann. chim. phys.*, 1859, [iii], 55, 293) was led to state that the dextrose from wood differs from all other dextroses.

The quantity of dextrose which is usually said to be obtainable from a given weight of cellulose is largely in excess of that observed by the author; such statements, however, are generally based merely on the reducing power of the product of hydrolysis, whereas in the solutions obtained, substances other than dextrose are present which are capable of reducing considerable quantities of Fehling's solution.

The portion of the product of hydrolysis which is insoluble in alcohol is usually regarded as 'dextrin,' but its high reducing power suggests the presence of a sugar analogous to *isomaltose*. If, however, pure dextrose is treated with sulphuric acid under conditions similar to those observed in the hydrolysis of wood, a part of the residue obtained is insoluble in alcohol, and resembles the 'dextrin' from wood; it may be, therefore, that in each case some of the dextrose is converted by the alcohol into the insoluble dextrose anhydride.

The difficulties attending the study of the hydrolysis of cellulose are greatly increased by the reversion of dextrose to dextrin which may occur in the process.

E. G.

Formation of Amino-alcohols. By LOUIS HENRY (*Ber.*, 1900, 33, 3169—3171. Compare this vol., i, 16, and Strauss, *ibid.*, 17).—A number of amino-alcohols have been prepared by the reduction of the corresponding nitro-compounds with tin and hydrochloric acid, or from cyano-alcohols by reduction with sodium and alcohol. They are somewhat viscid liquids with a fishy odour, and dissolve in water, but, with the exception of methyl- α -aminoethylcarbinol, are insoluble in ether:

| | Boiling point. | Sp. gr. |
|---|----------------|--------------|
| β -Aminoethyl alcohol, OH·CH ₂ ·CH ₂ ·NH ₂ | 171° | 1·022 at 20° |
| γ -Aminopropyl alcohol, OH·[CH ₂] ₃ ·NH ₂ | 187—188 | 1·020 at 12 |
| δ -Aminobutyl alcohol, OH·[CH ₂] ₄ ·NH ₂ | 206 | 0·967 at 12 |
| β -Aminoisopropyl alcohol, OH·CHMe·CH ₂ ·NH ₂ | 160—161 | 0·973 at 18 |
| Methyl- α -aminoethylcarbinol, OH·CHMe·CHMe·NH ₂ | 159—160 | 0·9423 at 18 |

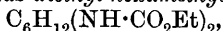
When nitroacetone is kept for some time it turns brown, whereas nitroethyl alcohol remains colourless even when kept for some years.

J. J. S.

Hydrazides and Azoimides of Organic Acids. XVII. Synthesis of $\alpha\gamma$ -Diaminopropane and $\alpha\zeta$ -Diaminohexane from Glutaric and Suberic Acids respectively. By THEODOR CURTIUS and HANS CLEMM (*J. pr. Chem.*, 1900, [ii], 62, 189—211).—*Glutaric dihydrazide*, CH₂(CH₂·CO·NH·NH₂)₂, obtained by boiling hydrazine hydrate with ethyl glutarate, crystallises in silky leaflets which melt at 176°, reduces Fehling's solution, forms a colourless *hydrochloride*, and when shaken with benzaldehyde yields *dibenzylideneglutaric dihydrazide*, which crystallises from glacial acetic acid in small needles melting at 231—232°. *Glutaric diazoimide*, CH₂(CH₂·CO·N₃)₂, is obtained by adding a cold solution of sodium nitrite to a cooled solution of

glutaric dihydrazide hydrochloride under ether; it is a clear, mobile, explosive oil with a suffocating odour, does not solidify at -15° , is decomposed by sodium hydroxide, yielding sodium azoimide; when treated with ethyl alcohol, it yields *diethyl trimethylenecarburethane*, $\text{CH}_2(\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2$, which is a viscous oil boiling and decomposing at $290-300^{\circ}$, and solidifying to feathery crystals after standing in a freezing mixture for some time; when heated in a sealed tube at $100-110^{\circ}$ for some hours, it yields trimethylenediamine hydrochloride. Glutaric diazoimide, when slightly warmed with water, explodes with the formation of small quantities of *trimethylenecarbamide* which melts at about 250° .

The corresponding suberic compounds were obtained by analogous methods. *Suberic dihydrazide*, $\text{C}_2\text{H}_4(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$, crystallises in large, colourless, lustrous leaflets which melt at $185-186^{\circ}$, and yields a *dibenzylidene* compound which crystallises in small, white needles and melts at 197° . *Suberic diazoimide* is obtained in compact crystals which melt at 25° and explode when heated further; when treated with alcoholic ammonia, it yields *suberamide*, which crystallises from alcohol and melts at 216° ; when treated with aniline, it yields *hexamethylenedicarbaniide*, $\text{C}_6\text{H}_{12}(\text{NH}\cdot\text{CO}\cdot\text{NHPh})_2$, which crystallises in long, thin, colourless prisms and melts at 220° ; when treated with anhydrous alcohol, it yields *diethyl hexamethylenediurethane*,



which crystallises in long, lustrous, colourless needles melting at 84° ; with alcohol in the presence of water, it yields the *urethanecarbamide*, $\text{CO}(\text{NH}\cdot[\text{CH}_2]_6\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2$, which is a colourless, crystalline compound melting at 132° ; when treated with water, it yields *hexamethylenecarbamide*, which crystallises in long, lustrous, colourless needles melting at 84° . $\alpha\zeta$ -*Diaminohexane dihydrochloride*, $\text{C}_6\text{H}_{12}(\text{NH}_2)_2\cdot 2\text{HCl}$, best prepared by the hydrolysis of diethyl hexamethylenediurethane with concentrated hydrochloric acid, crystallises in colourless needles, melts at 248° , and when treated with solid potash yields $\alpha\zeta$ -*diaminohexane* (hexamethylenediamine), which crystallises in silky, colourless leaflets, melts at 42° , boils at 100° under a pressure of 20 mm., is very hygroscopic, and absorbs carbon dioxide with the formation of a carbonate; it forms a *diacetyl* derivative which crystallises in small needles melting at $125-126^{\circ}$, a *dibenzoyl* derivative which crystallises in colourless plates melting at $157-158^{\circ}$, a *picrate*, $\text{C}_6\text{H}_{16}\text{N}_2\cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, which decomposes at about 200° , an *oxalate*, $\text{C}_6\text{H}_{16}\text{N}_2\cdot 2\text{H}_2\text{C}_2\text{O}_4\cdot \text{H}_2\text{O}$, which melts and decomposes at 168° , a *platinichloride*, $\text{C}_6\text{H}_{16}\text{N}_2\cdot \text{H}_2\text{PtCl}_6$, which decomposes between 222° and 224° , an *aurichloride* which crystallises in long, compact, lustrous yellow prisms, and a *mercurichloride*, $\text{C}_6\text{H}_{16}\text{N}_2\cdot 2\text{HCl}\cdot 4\text{HgCl}_2$, which crystallises in long leaflets and melts at $228-230^{\circ}$, all of which are analogous to the salts and derivatives of pentamethylenediamine; it dissolves uric acid, and has a very similar physiological action to piperazine and urotropine.

The melting points of the diamines, like those of the dibasic acids, of the normal hydrocarbons containing an even number of carbon atoms are higher than those containing an uneven number, whilst the boiling points increase regularly with number of carbon atoms.

R. H. P.

Hydrazides and Azoimides of Organic Acids. XVIII. Synthesis of $\alpha\beta$ -Diaminooctane from the Azide of Sebacic Acid.

By THEODOR CURTIUS and WILHELM STELLER (*J. pr. Chem.*, 1900, [ii], 62, 212—231).—*Sebacic dihydrazide*, $C_8H_{16} \cdot [CH_2]_3 \cdot CO \cdot NH \cdot NH_2)_2$, obtained by the action of hydrazine hydrate on diethyl sebacate, crystallises in lustrous, rhombic leaflets, melts at $184-185^\circ$, and when dry hydrogen chloride is passed into its anhydrous alcoholic solution, yields a *dihydrochloride* which forms rhombic crystals melting and decomposing about 250° ; it condenses with benzaldehyde, forming *dibenzylidenesebacic dihydrazide*, which melts at $158-159^\circ$, forms a *tetrabenzoyl* derivative which melts at 250° , and when treated with an alcoholic solution of iodine (2 mols. iodine to 5 mols. dihydrazide)

yields *s*-sec-sebacic hydrazide, $C_8H_{16} \begin{matrix} \diagup CO \cdot NH \\ \diagdown CO \cdot NH \end{matrix}$, which crystallises from alcohol and melts at 142° . *Sebacic diazoimide*, $C_8H_{16}(CO \cdot N_3)_2$, obtained by the action of nitrous acid on the dihydrazide, is a stable, colourless compound, which melts at $33-34^\circ$, and is not explosive. When treated with aniline, it yields *octomethylene dicarbamanilide*, $C_8H_{16}(NH \cdot CO \cdot NH \cdot Ph)_2$, which crystallises in flat, right-angled needles melting at $206-207^\circ$; when treated with water, *octomethylenecarbamide* is formed, which is an insoluble, bluish-white powder decomposing at 216° ; when treated with moist ethyl alcohol, *s*-dioctomethylenediethylurethanecarbamide, $CO(NH \cdot [CH_2]_8 \cdot NH \cdot CO_2Et)_2$, is obtained as an amorphous compound melting at $132-133^\circ$; when treated with absolute ethyl alcohol, *diethyloctomethylenediurethane*, $C_8H_{16}(NH \cdot CO_2Et)_2$, is formed, and crystallises in feathery aggregates melting at $78-80^\circ$; when treated with methyl alcohol, the corresponding *dimethylurethane* which melts at $114-115^\circ$ is obtained.

Octomethylenediamine dihydrochloride is best prepared by boiling either the diethyl- or dimethyl-urethane with concentrated hydrochloric acid for six hours. The derivatives and salts of octomethylenediamine are analogously constituted to those of hexamethylenediamine (see preceding abstract); the *dibenzoyl* derivative crystallises in silky prisms and melts at 140° , the *picrate* melts at $182-183^\circ$, the *oxalate* crystallises in lustrous, white laminæ and melts at 223° , the *mercurichloride* crystallises in pinkish aggregates and melts at $189-191^\circ$, the *aurichloride* forms microscopic crystals and melts at $188-189^\circ$; it also forms a characteristic salt with cadmium chloride, which crystallises in white aggregates from hydrochloric acid, and does not melt below 300° . When treated with nitrous acid, the diamine yields a greenish oil, which has the odour of octyl alcohol, and is probably *octomethyleneglycol*.
R. H. P.

Hydrazides and Azoimides of Organic Acids. XIX. Synthesis of $\alpha\beta\gamma$ -Triaminopropane from Tricarballic Acid.

By THEODOR CURTIUS and AUGUST HESSE (*J. pr. Chem.*, 1900, [ii], 62, 232—246).—*Tricarballic trihydrazide*, $C_3H_5(CO \cdot NH \cdot NH_2)_3$, obtained by the action of hydrazine hydrate on triethyl tricarballylate, is a crystalline substance melting at $195-196^\circ$, and forms a very soluble *trihydrochloride*, which melts and decomposes at 148° , a *tripicrate* which crystallises in small, yellow plates and melts at 173° , and condensation

products with benzaldehyde and salicylaldehyde, which are white, microcrystalline substances melting at 218° and $205\text{--}206^{\circ}$ respectively; when treated with nitrous acid, it yields *tricarballic triazomide*, $\text{C}_3\text{H}_5(\text{CO}\cdot\text{N}_3)_3$, which is a clear, explosive oil; this, when treated with anhydrous ethyl alcohol, yields *triethyl glyceryltriurethane*, $\text{C}_3\text{H}_5(\text{NH}\cdot\text{CO}_2\text{Et})_3$, which melts at $91\text{--}92^{\circ}$; when treated with water, *diglycerylcarbamide*, $\text{CO}(\text{NH}\cdot\text{C}_3\text{H}_5\text{---}\text{NH}\text{---}\text{CO})_2$, which is a white, crystalline substance, is formed.

$\alpha\beta$ -*Triaminopropane*, $\text{C}_3\text{H}_5(\text{NH}_2)_3$ (compare Gabriel and Michels, Abstr., 1893, i, 31), is a colourless oil which boils at $92\text{--}93^{\circ}$ under 9 mm. pressure, and forms a *trihydrochloride*, which is obtained by the hydrolysis of the urethane with hydrochloric acid, crystallises, with H_2O , in colourless, compact plates, and, when anhydrous, begins to sinter at 220° , and melts and decomposes about 250° ; it forms an *aurichloride*, $\text{C}_3\text{H}_5(\text{NH}_2)_3\cdot 3\text{HCl}\cdot\text{AuCl}_3$, which melts and decomposes at $210\text{--}212^{\circ}$, a *platinichloride*, $\text{C}_3\text{H}_5(\text{NH}_2)_3\cdot 3\text{HCl}\cdot\text{PtCl}_4$, which crystallises in needles and decomposes at 220° , a *tripicrate*, which crystallises in long, yellow needles and does not melt below 270° , and a *tribenzoyl* derivative, which is a microcrystalline substance melting at $206\text{--}207^{\circ}$, and is particularly suited for the purification of the base, as when hydrolysed with strong hydrochloric acid it yields the hydrochloride in a pure state.

R. H. P.

Formation of Canarin. By BRONISLAW PAWLEWSKI (*Ber.*, 1900, 33, 3164).—Pure canarin is readily formed when ammonium persulphate is added gradually to a solution of ammonium thiocyanate contained in an open dish. When a woollen fabric is dipped in ammonium persulphate solution and then in ammonium thiocyanate and the operations repeated several times, the fabric becomes dyed intensely with canarin.

J. J. S.

A Method of Preparing Hydantoin. By CARL D. HARRIES and MAURUS WEISS (*Ber.*, 1900, 33, 3418—3449).—The hydrochloride of the ethyl ester of glycine, when treated with potassium cyanate, is converted into *ethyl hydantoate*, which crystallises in compact needles, melts at 135° , and when treated with nitrous acid yields a *nitroso*-derivative melting at $66\text{--}67^{\circ}$; this ester, when heated at 135° for seven hours, or when warmed with 25 per cent. hydrochloric acid, is converted into hydantoin. The hydantoin formed by the latter method melts at $217\text{--}220^{\circ}$ instead of at 215° . Quantitative yields are obtained in all the stages from glycine.

R. H. P.

Electrolytic Reduction of Methyluracil. By JULIUS TAFEL and ARTHUR WEINSCHENK (*Ber.*, 1900, 33, 3378—3383).—Methyluracil, $\text{CO}\text{---}\text{NH}\cdot\text{CMe}\text{---}\text{NH}\text{---}\text{CO}\text{---}\text{CH}$, was dissolved in 50 per cent. sulphuric acid and reduced electrolytically either at 15° or at 50° , between prepared lead electrodes (Abstr., 1900, ii, 588), with a current concentration of 120—150 amperes. The resulting liquid was freed from free sulphuric acid and evaporated under diminished pressure; the residue was extracted with boiling chloroform, in which *methyltrimethylene*-

carbamide, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CHMe} \\ \text{NH} - \text{CH}_2 \end{smallmatrix} > \text{CH}_2$, dissolved, whilst the sulphate of α -diaminobutane, $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$, remained behind. Methyltrimethylenecarbamide melts at $200-202^\circ$, and is neutral in reaction; it forms a *picrate*, which was analysed; it is not easily hydrolysed, but when heated with concentrated hydrochloric acid at 200° (or less well with 30 per cent. sulphuric acid), it loses carbon dioxide and forms diaminobutane. α -Diaminobutane boils at $140.5-141.5^\circ$ under 738 mm. pressure, and has a sp. gr. 0.86; its *hydrochloride*, which melts at $170-172^\circ$, and *picrate*, which is very insoluble and explodes when heated, were analysed.

These reactions afford a convenient means of preparing α -diaminobutane. Methyluracil is reduced electrolytically in the manner described; the resulting liquid is freed from so much sulphuric acid that three parts of the latter still remain for every 1 part of methyluracil, the liquid is concentrated until only 10 c.c. remain per 1 gram of uracil, and the residue is heated for 6 hours at 200° . C. F. B.

Electrolytic Reduction of Barbituric Acid. By JULIUS TAFEL and ARTHUR WEINSCHENK (*Ber.*, 1900, 33, 3383—3387).—Barbituric acid, or malonylcarbamide, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} > \text{CH}_2$, was reduced electrolytically at $16-21^\circ$, and the product worked up as in the case of methyluracil (preceding abstract). The residue after the evaporation contained trimethylenecarbamide, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CH}_2 \\ \text{NH} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH}_2$, and *hydrouracil*, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CH}_2 \\ \text{NH} - \text{CO} \end{smallmatrix} > \text{CH}_2$; the latter remained behind when the residue was extracted with cold water, whilst the trimethylenecarbamide dissolved, and could be recovered from the solution by means of its *picrate*, which is almost insoluble in cold water. Hydrouracil melts at 274° , and in small quantities sublimes unchanged; it does not dissolve more readily in dilute hydrochloric acid than in water, but it does so in aqueous sodium or barium hydroxide; from these solutions, it is precipitated by carbon dioxide. C. F. B.

Nitration of the Disubstitution Derivatives of Benzene. By CHARLES CLOEZ (*Compt. rend.*, 1900, 131, 899—901).—When a disubstitution derivative of benzene contains a basic group NH_2 or NR_2 , and the second group is neutral (Me, Cl) feebly acid (OH) or acid (CO_2H), nitration takes place in the para- or ortho-position with respect to the amino-group. Nitration in the meta-position is obtained only in presence of a large excess of sulphuric acid.

When the benzene derivative contains an OH group with the groups Me , Cl , NO_2 , or COH , nitration takes place in the ortho- and para-positions, but if the hydroxyl group is converted into an alkyloxy-group, nitration will take place also in the meta-position. With the derivatives $\text{CO}_2\text{H} : \text{OH} = 1 : 3$, three compounds are obtained with the NO_2 group in the position 2 or 4 or 5.

When the derivative contains a Me or Cl group with a NO_2 , CO_2H , or COH group, nitration takes place in the ortho- or para-position with respect to the Cl or Me group.

With *o*-nitro- or *p*-nitro-benzoic acid, the second nitration takes place in the meta- or para-position with respect to the first nitro-groups.

C. H. B.

Nitro-derivatives of *o*-Dinitrosotoluene and *o*-Dinitroso-xylene. By THEODOR ZINCKE and P. DROST (*Annalen*, 1900, 313, 299—316. Compare Abstr., 1899, i, 751).—*Nitro-o-dinitrosotoluene* [$\text{Me}:\text{NO}_2:(\text{NO})_2=1:2:3:4$ or $1:6:3:4$], prepared from 3:4-dinitrosotoluene and fuming nitric acid, crystallises in pale yellow needles which melt and decompose at 164° ; it is also formed when the imide of *o*-nitro-*p*-toluidine is added to fuming nitric acid and the product heated in a brine bath. 2:6-Dinitro-3:4-dinitrosotoluene, obtained by the action of fuming nitric acid on a solution of the nitro-derivative in concentrated sulphuric acid, crystallises from concentrated nitric acid in silky yellow needles melting and decomposing at 133° .

Nitro-o-dinitrosotoluene [$\text{Me}:(\text{NO})_2:\text{NO}_2=1:3:4:5$], produced when dinitro-*p*-diazotolueneimide is heated at 110° , crystallises from glacial acetic acid in lustrous, yellow leaflets melting at 145° ; dinitro-*p*-diazotolueneimide, formed on dissolving nitrodiazotolueneimide in fuming nitric acid, crystallises from alcohol in colourless needles and melts at 97° .

5-Nitro-2:3-dinitrosotoluene crystallises from alcohol in yellow leaflets and melts at 70° . 5-Nitro-*o*-diazotolueneimide [5-nitrotoluene-2-azoimide], $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_3$, melts at 69° , and when treated with fuming nitric acid is converted into 3:5-dinitrotoluene-5-azoimide, which crystallises from alcohol in pale yellow needles, and melts at 61° ; the latter substance yields 5-nitro-2:3-dinitrosotoluene when heated on the water-bath.

Nitrodinitrosotoluene [$\text{Me}:(\text{NO})_2:\text{NO}_2=1:2:3:4$], obtained by dissolving 2:3-dinitrosotoluene in fuming nitric acid, forms pale yellow, feathery crystals and melts at 162° ; a mixture of concentrated sulphuric and nitric acids converts it into dinitrodinitrosotoluene [$\text{Me}:(\text{NO})_2:(\text{NO}_2)_2=1:2:3:4:6$], which melts and decomposes at 122 — 123° .

Dinitro-*m*-xyleneazoimide [$\text{Me}_2:\text{N}_3:(\text{NO}_2)_2=1:3:4:5:6$ or $1:3:4:2:5$], produced by the action of fuming nitric acid on 3:4:5-nitro-*m*-xyleneazoimide, crystallises from alcohol in white leaflets melting at 82° ; when heated at 110° , it yields nitrodinitroso-xylene, which crystallises from alcohol in yellow needles, and melts at 116° .

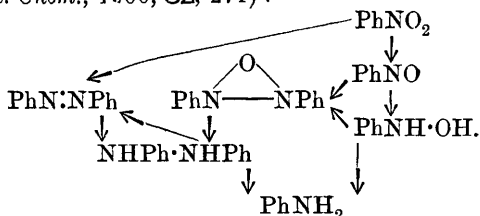
Nitrotolylenefurazan, $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{Me}\lessgtr\text{N}\text{>O}$, prepared from 1:3:4-tolylenefurazan and nitric acid, crystallises in long, yellowish needles, and melts at 83° .

Dinitroaminocresol [$\text{Me}:\text{OH}:(\text{NO}_2)_2:\text{NH}_2=1:2:3:5:4$], formed when dinitro-*p*-tolueneazoimide, is dissolved in concentrated sulphuric acid, crystallises from boiling water in small, red needles, and melts at 172° , when it decomposes; the acetyl derivative forms yellow crystals, and melts at 171° . Dinitroaminocresol [$\text{Me}:\text{OH}:(\text{NO}_2)_2:\text{NH}_2=1:4:3:5:2$ or $1:6:3:5:2$], obtained from dinitro-*o*-tolueneazoimide, crystallises from boiling water in small, yellow needles.

The compound $\text{C}_7\text{H}_7\text{O}_5\text{N}_3$, a bye-product of the nitration of nitro-*p*-tolueneazoimide, separates from alcohol in lustrous crystals, and

melts, decomposing, at 146° ; the *acetyl* derivative melts and evolves gas at 142° . M. O. F.

Electro-chemical Reduction of Mononitro-compounds in slightly Alkaline Solutions. By KARL ELBS (*Zeit. Electrochem.*, 1900, 7, 133 and 144).—The author gives a *résumé* of the results obtained in the reduction of 56 mononitro-compounds by the method described by him (*Abstr.*, 1899, i, 270). He shows that, in every case, these results are in harmony with the following representation of the electrolytic reduction of nitrobenzene, due to Haber and Schmidt (*Zeit. physikal. Chem.*, 1900, 32, 271):



The vertical arrows indicate electrolytic reductions, the slanting ones indicate purely chemical reactions which take place between the different products. The nature and relative quantities of the final products will, of course, depend on the properties of the compound undergoing reduction. *p*-Nitroaniline, for example, yields *p*-phenylenediamine, owing to the fact that the nitroso-compound first formed changes very readily into quinoneimide oxime, which can only lead to the diamine; *m*-nitroaniline, on the other hand, yields *m*-diaminoazobenzene, owing to the fact that the meta-compounds have no tendency to form quinone derivatives. The nitroso- and hydroxylamine compounds formed by the direct reduction, therefore, react yielding the azoxy-compound which is further reduced.

The azo-compound is always formed by oxidation of the hydrazo-compound; in cases, therefore, where the latter is not readily formed the azo-compound is not produced.

The dinitro-compounds behave in an entirely different manner.

T. E.

Isolation of Sulphonic Acids by Vacuum Distillation. By FRIEDRICH KRAFFT and W. WILKE (*Ber.*, 1900, 33, 3207—3209. Compare Krafft and Roos, *Abstr.*, 1892, 1219).—In addition to the sulphonic esters, a number of sulphonic acids can be purified by distillation, when the cathode-light vacuum is used (*Abstr.*, 1896, ii, 464). The boiling points and melting points of the acids are as follows:

| | M. p. | B. p. at 0 mm. | Height of vapour column. |
|--|-------|-------------------|-----------------------------|
| Benzenesulphonic acid | 66° | 135° | 90 mm. |
| Toluene- <i>p</i> -sulphonic acid | 35 | 147 | 65 " |
| <i>p</i> -Xylenesulphonic acid..... | 48 | 149 | 55 " |
| <i>p</i> -Chlorobenzenesulphonic acid... | 68 | 148 | 60 " |
| <i>p</i> -Bromobenzenesulphonic acid... | 103 | 155 | 60 " |

T. M. L.

$\alpha\beta$ -Dichlorostyrenes and some Acetylenes. By FRANZ KUNCKELL and R. KORITZKY (*Ber.*, 1900, 33, 3261—3264. Compare Abstr., 1900, i, 638).— **$\alpha\beta$ -Dichloro-*p*-ethylstyrene**, $C_6H_4Et \cdot CCl:CHCl$, prepared by heating chloroacetyl-*p*-ethylbenzene with phosphorus pentachloride, is a colourless oil boiling at 265° ; it has a sp. gr. 1.2565 at 17° . ***p*-Ethylphenylchloroacetylene**, $C_6H_4Et \cdot C:CCl$, obtained by boiling the preceding compound with alcoholic potassium hydroxide, is a yellow oil with an odour of oranges boiling at 160 — 170° under 35 mm. pressure; it has a sp. gr. 1.0871 at 17° . ***p*-Ethylphenylacetylene**, $C_6H_4Et \cdot C:CH$, readily produced by treating $\alpha\beta$ -dichloro-*p*-ethylstyrene with sodium in ethereal solution, possesses an odour of anise, boils at 110° under 10 mm. pressure and has a sp. gr. 0.9086 at 18° .

***p*-Cumyl chloromethyl ketone**, which crystallises from alcohol in needles and melts at 55 — 56° , yields **$\alpha\beta$ -dichloro-*p*-isopropylstyrene**, a colourless oil boiling at 190 — 200° under 23 mm. pressure and having a sp. gr. 1.2736 at 17° .

***p*-isopropylphenylchloroacetylene**, $CHMe_2 \cdot C_6H_4 \cdot C:CCl$, a yellow oil boiling at 170 — 180° under 30 mm. pressure, has a sp. gr. 1.0852 at 17° . ***p*-isopropylphenylacetylene**, a liquid having an ethereal odour, boils at 110 — 120° under 10 mm. pressure and has a sp. gr. 0.9124 at 17° . **$\alpha\beta$ -Dichloro-2 : 4 : 6-trimethylstyrene**, $C_6H_2Me_3 \cdot CCl:CHCl$, is a colourless oil boiling at 285 — 289° under atmospheric pressure; it has a sp. gr. 1.1998 at 17° .

2 : 4 : 6-Trimethylphenylchloroacetylene, $C_6H_2Me_3 \cdot C:CCl$, a pale yellow oil boiling at 180 — 190° under 20 mm. pressure, has a sp. gr. 1.0349 at 18° . **2 : 4 : 6-Trimethylphenylacetylene**, $C_6H_2Me_3 \cdot C:CH$, has an ethereal odour and boils at 168 — 175° under 20 mm. pressure; it has a sp. gr. 0.8731 at 17° .

***Cymyl* chloromethyl ketone**, $CHMe_2 \cdot C_6H_3Me \cdot CO \cdot CH_2Cl$, crystallises from alcohol in needles and melts at 18 — 20° . **$\alpha\beta$ -Dichloro-2 (or 5)-methyl-5 (or 2)-isopropylstyrene**, $CHMe_2 \cdot C_6H_3Me \cdot CCl:CHCl$, obtained from the preceding ketone, is a colourless oil boiling at 268° under atmospheric pressure and having a sp. gr. 1.1296. **2 (or 5)-Methyl-5 (or 2)-isopropylphenylchloroacetylene**, $CHMe_2 \cdot C_6H_3Me \cdot C:CCl$, a yellow oil, boils at 215° under 40 mm. pressure and has a sp. gr. 1.0512 at 17° . **2 (or 5)-Methyl-5 (or 2)-isopropylphenylacetylene**, $CHMe_2 \cdot C_6H_3Me \cdot C:CH$, boils at 128 — 130° under 50 mm. pressure and has a sp. gr. 0.8882 at 17° .

The sodium derivatives of the above unchlorinated acetylene, obtained in ethereal solution, are very unstable substances, being decomposed even by rubbing on a porous tile; water converts them into the corresponding acetylene and sodium hydroxide.

G. T. M.

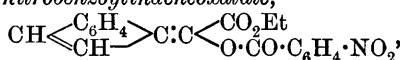
Some Chloromethoxystyrenes. By FRANZ KUNCKELL and K. ERAS (*Ber.*, 1900, 33, 3264—3265. Compare preceding abstract).— **$\alpha\beta$ -Dichloro-*p*-methoxystyrene**, $OMe \cdot C_6H_4 \cdot CCl:CHCl$, prepared from chloroacetylanisole and phosphorus pentachloride, is a colourless oil boiling at 155° under 12 mm. and at 268° under atmospheric pressure; it solidifies on cooling and has a sp. gr. 1.291 at 18° .

Bisdichloroethyleneanisole, $OMe \cdot C_6H_3(CCl:CHCl)_2$, obtained from di-

chloroacetylanisole boils at 160—170° under 17 mm. pressure and has a sp. gr. 1.460 at 21°.

In the case of these methoxystyrenes, the removal of hydrogen chloride by alcoholic potash takes place only in sealed tubes; sodium fails to withdraw the halogen atoms even at the temperature of the water-bath. G. T. M.

Condensation Products of Indene. By JOHANNES THIELE (*Ber.*, 1900, 33, 3395—3401).—The so-called condensation product obtained by Marckwald (*Abstr.*, 1895, i, 535) from indene and benzaldehyde is shown to be the additive product hydroxybenzylbenzylideneindene, $C_{23}H_{18}O$, and Marckwald's acetate, produced by the action of acetyl chloride, is its chloro derivative, $C_{23}H_{17}Cl$, which with moist silver oxide yields the hydroxy-compound, and when reduced with zinc dust and acetic acid yields a colourless, crystalline compound, $(C_{23}H_{18})_x$, which melts at 212—213°, and is probably a polymeride of benzylbenzylideneindene. *Benzylideneindene*, $CH \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown CH \end{smallmatrix} > C:CHPh$, obtained in small quantities by the condensation of benzaldehyde and indene in the presence of alcoholic potash, crystallises in yellow leaflets, melts at 88°, and with concentrated sulphuric acid gives a yellowish-green coloration. Indene and cinnamaldehyde condense readily in the presence of alcoholic potash, with the formation of *cinnamylideneindene*, $CH \begin{smallmatrix} \diagup CH \\ \diagdown C_6H_4 \end{smallmatrix} > C:CH \cdot CH:CHPh$, which crystallises in yellowish-red needles, melts at 190°, and gives a brown coloration with concentrated sulphuric acid, and an additive compound, $C_{27}H_{22}O$, which is analogous to hydroxybenzylbenzylideneindene, crystallises in slender, yellow needles, melts at 160—161°, and gives a green coloration with sulphuric acid. Ethyl indeneoxalate and *p*-nitrobenzoyl chloride condense in acetone solution in the presence of pyridine, forming *ethyl p-nitrobenzoylindeneoxalate*,



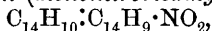
which is a yellow, crystalline compound melting at 113—114°; the corresponding *benzoyl* compound is a red oil. *Indeneoxalic acid*, obtained by the careful hydrolysis of the condensation product of ethyl oxalate and indene, crystallises in small, lustrous, red prisms and melts and decomposes at 153—154°. R. H. P.

The Phenanthrene Series: Action of Nitrous Acid on Phenanthrene. By JULIUS SCHMIDT (*Ber.*, 1900, 33, 3251—3260).—*Nitro-dihydrophenanthrene oxide*, $O(C_{14}H_{10} \cdot NO_2)_2$, obtained in colourless, cubical crystals by saturating a benzene solution of phenanthrene with the fumes evolved from arsenious oxide and nitric acid, melts at 154—155°; it is extremely insoluble in the organic solvents, and, when recrystallised from benzene, separates in transparent prisms containing 1 mol. of benzene and melting at 134—135°. The substance gives the Liebermann reaction for nitroso-compounds, and on treatment with sodium methoxide yields a *nitrophenanthrene* melting

at 116—117°, which is not identical with the mononitro-derivatives obtained by the direct nitration of the hydrocarbon.

Bismononitrodihydrophenanthrene, $\text{NO}_2 \cdot \text{C}_{14}\text{H}_{10} \cdot \text{C}_{14}\text{H}_{10} \cdot \text{NO}_2$, which separates from the benzene mother liquor in the preceding experiment, consists of small needles melting at 199—200°, and crystallises from alcohol in pyramidal prisms; it also gives the Liebermann reaction, and develops a brownish-green coloration with cold concentrated sulphuric acid, which becomes deep green on warming, and changes to yellowish-brown on the addition of alkali.

Mononitrobisphenanthran (*mononitrobisdihydrophenanthrylene*),



produced by heating the preceding compound for 10 minutes at 200—205°, crystallises from benzene in lustrous, yellow prisms and melts at 210—212°. The author proposes to employ the term “phenanthran” for the bivalent radicle, $\text{C}_{14}\text{H}_{10}$, derived from dihydrophenanthrene, and the preceding compound is named in accordance with this nomenclature.

Dinitrobisphenanthran, $\text{NO}_2 \cdot \text{C}_{14}\text{H}_9 : \text{C}_{14}\text{H}_9 \cdot \text{NO}_2$, results from the action of sodium ethoxide on bismononitrodihydrophenanthrene; it slowly decomposes at 300° and has not been obtained crystalline owing to its insolubility in the ordinary solvents. G. T. M.

Preparation of Triphenylchloromethane. By MOSES GOMBERG (*Ber.*, 1900, 33, 3144—3149; *J. Amer. Chem. Soc.*, 1900, 22, 752—757. Compare E. and O. Fischer, *Abstr.*, 1879, 384).—The triphenylmethane obtained by so many authorities by the action of benzene on carbon tetrachloride in the presence of aluminium chloride is due to a secondary decomposition of the triphenylchloromethane, which is the first product formed. A 70—87 per cent. yield of the latter may be obtained by heating together carbon tetrachloride, benzene, and aluminium chloride, and at the end of the reaction running the well cooled mixture on to a large quantity of powdered ice contained in a vessel surrounded by a good freezing mixture.

For a good yield, it is essential that the original substances should be thoroughly dry, and that the product should never be left in contact with water for any length of time. J. J. S.

Triphenylmethyl. An Instance of Tervalent Carbon. By MOSES GOMBERG (*Ber.*, 1900, 33, 3150—3163; *J. Amer. Chem. Soc.*, 1900, 22, 757—771).—Triphenyl-bromo- or -chloro-methane is not acted on by metallic sodium, but zinc, mercury, or “molecular” silver remove the bromine or chlorine and, in the absence of air the unsaturated hydrocarbon *triphenylmethyl*, CPh_3 , is quantitatively formed, but when air is not completely excluded, a considerable amount of *triphenylmethyl peroxide*, $\text{CPh}_3 \cdot \text{O} \cdot \text{O} \cdot \text{CPh}_3$, is produced.

The author recommends the action of pure powdered zinc on a benzene solution of the chloro-compound, the operation being conducted in an apparatus free from rubber or cork connections. When the benzene solution is concentrated at 30—35° in an atmosphere of dry carbon dioxide, a solid residue of the unsaturated hydrocarbon is left; it does not melt at 60°, dissolves readily in benzene or carbon disulphide, and when a solution is kept for several weeks large, transparent crystals

are deposited ; it has not been found possible to obtain these in a pure form, as they rapidly absorb oxygen.

Triphenylmethyl peroxide is readily produced when the hydrocarbon is left exposed to the atmosphere, when air is aspirated through a benzene solution of the hydrocarbon, or when the benzene solution is treated with an aqueous solution of sodium peroxide. It is only sparingly soluble in the usual solvents, but may be crystallised from chloroform or carbon disulphide in the form of six-sided plates melting at $185-186^{\circ}$; it is stable in the air but slowly decomposes when its solutions are boiled. When dissolved in cold concentrated sulphuric acid, it gives a yellow solution which quickly darkens, and on dilution triphenylcarbinol is precipitated. When nitrated, it yields *hexanitrotriphenylmethyl peroxide*, $O_2[C(C_6H_4 \cdot NO_2)_3]_2$, melting at 210° and sparingly soluble in most solvents.

Triphenyliodomethane, CPh_3I , is readily obtained when a carbon disulphide solution of the unsaturated hydrocarbon is treated at 0° with a solution of iodine in the same solvent, and is best isolated in an atmosphere of dry carbon dioxide. It is unstable, readily darkens and loses iodine, melts at about 135° , and by water, especially in the presence of alkalis, is transformed into the carbinol; boiling with alcohol converts it into triphenylmethane. The corresponding bromo- and chloro-compounds cannot be obtained by a similar process as bromine and chlorine form substitution as well as additive products.

J. J. S.

Action of Ethyl Acetonedicarboxylate on Aniline. By EMIL BESTHORN and E. GARBEN (*Ber.*, 1900, 33, 3439—3447).—*Ethyl- β -anilinogluconate*, $CO_2Et \cdot CH_2 \cdot C(NHPh) : CH \cdot CO_2Et$, prepared by the interaction of aniline and ethyl acetonedicarboxylate at the ordinary temperature, crystallises from methyl alcohol in transparent crystals melting at 87° , but melts at $97-98^{\circ}$ when crystallised several times from dry ether; the variation in melting point is explained by the supposition that two isomerides are produced; the ester is insoluble in water but soluble in organic solvents, gives a yellowish-brown coloration with aqueous alcoholic ferric chloride, and is hydrolysed by cold dilute mineral acids.

Three products are formed when ethyl acetonedicarboxylate is heated with aniline in a sealed tube at 100° . *Acetonedicarboxydianilide*, $CO(CH_2 \cdot CO \cdot NHPh)_2$, crystallises from absolute alcohol in small, colourless needles, melts, evolving gas, at 155° , gives a violet coloration with ferric chloride, and dissolves without decomposition in cold dilute sodium carbonate; concentrated sulphuric acid gives sulphanilic acid, but the anilide condenses in presence of 80 per cent. acid on the water-bath to 2-quinolone-4-acetic acid. The *monoanilide* of *ethyl- β -anilinogluconate*, $NHPh \cdot CO \cdot CH_2 \cdot C(NHPh) : CH \cdot CO_2Et$, separates from methyl alcohol in well-formed crystals, and when crystallised from dry ether melts at $129-130^{\circ}$; with ferric chloride, it gives a yellowish colour, rapidly passing to violet as the compound is hydrolysed by the acid of the ferric chloride. The *monoanilide* of *ethyl acetonedicarboxylate*, $NHPh \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO_2Et$, which is best prepared by the action of cold dilute hydrochloric acid on the preceding compound, crystallises from dry ether, melts at $75-76^{\circ}$, dissolves

slightly in hot water and separates on cooling in minute felted needles; it dissolves unchanged in cold dilute sodium hydroxide, and can be reprecipitated at first by carbon dioxide, but hydrolysis of the ester gradually takes place; it is converted into 2-quinolone-4-acetic acid by warming with concentrated sulphuric acid during 2 hours on the water-bath.

2-Quinolone-4-acetic acid, $\begin{matrix} \text{NH}\cdot\text{C}_6\text{H}_4 \\ | \\ \text{CO}-\text{CH} \end{matrix} \gg \text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is only slightly soluble in water and organic solvents, crystallises from hot water in white, felted needles, melts, evolving gas, at $205-206^\circ$, and by further heating is converted completely into lepidone and carbon dioxide. The ethyl ester, $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}$, crystallises from benzene in colourless, flat needles, melts at $172-173^\circ$, and forms soluble crystalline salts with mineral acids. T. M. L.

Anilides of Alkylsulphonacetic Acids. By W. GROTHE (*Arch. Pharm.*, 1900, 238, 587—600).—Chloroacetyl derivatives of amines, $\text{NHR}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, were prepared by mixing chloroacetic acid with the amine and cooling well, after which the product was mixed with excess of phosphoric oxide. In the case of methylaniline, chloroacetyl chloride was added to the well-cooled amine; indeed, this method is preferable in all cases for work on any but quite a small scale. There were prepared (the temperatures given are melting points): the chloroacetyl derivatives of aniline; *o*- and *p*-toluidine; 1:3:4-*xyloidine*, 109° ; 1:2:5-*xyloidine*, 153° ; *p*-phenetidine, 148° ; methylaniline, 70° .

These chloroacetyl derivatives form sulphonacetyl compounds, $\text{NHR}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{R}'$, when boiled with sodium benzene- or *p*-toluenesulphinate in alcoholic solution. When these compounds are boiled with 10 per cent. alcoholic potash, they are hydrolysed in all cases to the amine, NH_2R , carbon dioxide, and a sulphone, $\text{CH}_3\cdot\text{SO}_2\cdot\text{R}'$. Those prepared are: the phenylsulphonacetyl and *p*-tolylsulphonacetyl derivatives of aniline, 142° and 168° respectively; *o*-toluidine, 150° and 129° ; *p*-toluidine, 153° and 157° ; 1:3:4-*xyloidine*, 141° and $153-154^\circ$; 1:2:5-*xyloidine*, 143° and 160° ; *p*-phenetidine, 151° and 156° ; methyl-aniline, 125° and 112° . C. F. B.

Action of Potassium Hydrosulphide, Potassium Cyanide, and Potassium Thiocyanate on Chloroacetanilides. By W. GROTHE (*Arch. Pharm.*, 1900, 238, 600—614).—When potassium hydrosulphide is added gradually to a chloroacetanilide, $\text{NHR}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, both in alcoholic solution, a dianilide of thiodiglycollic acid, $(\text{NHR}\cdot\text{CO}\cdot\text{CH}_2)_2\text{S}$, is obtained. In this way were prepared (the numbers given are melting points): thiodiglycollyl derivatives of aniline; *o*-toluidine, 190° ; *p*-toluidine, 194° ; 1:3:4-*xyloidine*, 194° ; 1:2:5-*xyloidine*, 210° ; *p*-phenetidine, 221° ; methylaniline, 115° .

By oxidation with potassium permanganate in acetic acid solution, these derivatives can be converted into sulphones, $(\text{NHR}\cdot\text{CO}\cdot\text{CH}_2)_2\text{SO}_2$; the yield is not always good, however. There were prepared: sulphonodiacetyl derivatives of aniline, $220-225^\circ$; *o*-toluidine, $225-226^\circ$; *p*-toluidine, 221° ; 1:2:5-*xyloidine*, 237° ; *p*-phenetidine, 239° ; methyl-aniline, 152° ; from 1:3:4-*xyloidine* the corresponding derivative could not be obtained.

By mixing the chloroacetanilides with potassium cyanide in aqueous alcoholic solution, cyanoacetanilides, $\text{NHR} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CN}$, can be obtained in some cases. There were prepared: *cyanoacetyl* derivatives of aniline; *p-toluidine*, 180° ; *1:2:5-xylydine*, 167° ; methylaniline; the corresponding derivatives of *o-toluidine*, $1:3:4\text{-xylydine}$, and *p-phenetidine* could not be obtained. When these derivatives are heated with hydrochloric or sulphuric acid, they are hydrolysed to the amine, NH_2R , carbon dioxide, acetic acid, and ammonia.

When chloroacetanilides are heated with potassium thiocyanate in alcoholic solution, they form thiocyanacetanilides, $\text{NHR} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{SCN}$. There were prepared: *thiocyanoacetyl* derivatives of aniline, $86\text{--}87^\circ$; *o-toluidine*, $102\text{--}103^\circ$; *p-toluidine*, $125\text{--}126^\circ$; *1:3:4-xylydine*, 102° ; *1:2:5-xylydine*, 133° ; *p-phenetidine*, $164\text{--}165^\circ$; *methylaniline*, 69° .
C. F. B.

Action of Potassium Thiocyanate on Chloroacetanilides. By GUSTAV FRERICHs and HEINRICH BECKURTS (*Arch. Pharm.*, 1900, 238, 615—616).—The thiocyanacetyl compounds prepared by Grothe (preceding abstract) are derived from thiocyanacetic acid, with the exception of the methylanilide, which is derived from thiocarbiminoacetic acid. The products obtained from other secondary amines, for instance ethylaniline, are also thiocarbimino-derivatives. Compounds of primary amines with thiocarbiminoacetic acid, on the other hand, are very unstable. In one case, that of *thiocarbiminoacetyl-p-toluidide*, the compound could be prepared by allowing potassium thiocyanate to act on chloroacetyl-*p-toluidide* in alcoholic solution for a very short time only; if the solution is heated, this compound is transformed into *thiocyanoacetyl-p-toluidide*, which finally can be converted into *p-tolyl-thiohydantoin*.
C. F. B.

Some Reactions of Substituted Anilines. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1900, 131, 945—946).—In this paper, a minute description is given of the various colour changes and precipitates produced when solutions of methylaniline, dimethylaniline, ethylaniline, and diethylaniline in 97 per cent. alcohol are mixed with dilute or concentrated solutions of cupric chloride, sulphate, or acetate, and also, in the case of methylaniline, with solutions of cobalt or nickel chloride.
N. L.

Trinitrothymol and its Derivatives. By GUIDO MALDOTTI (*Gazzetta*, 1900, 30, ii, 365—370).—Trinitrothymol, prepared by Lallemand (*Ann. Chim. Phys.*, 1857, [iii], 49, 150), has the normal molecular weight in freezing phenol. The following derivatives have been prepared. The *benzoyl* compound, $\text{OBz} \cdot \text{C}_6\text{MePr}(\text{NO}_2)_3$, separates from alcohol in silky, pale yellow needles melting at 140° and boiling and decomposing at 250° ; it dissolves slightly in water or light petroleum, and is very soluble in benzene, in which its cryoscopic behaviour is normal. The *acetyl* derivative crystallises from benzene in pale yellow scales or plates melting at 135° ; it dissolves slightly in ether, more readily in light petroleum, and gives the normal molecular weight in benzene. The *ethyl* derivative is deposited from alcohol in rhomboidal, nacreous scales or rectangular prisms which

melt at 75° ; it is soluble in benzene, to which it gives the normal depression of freezing point. The *phenylhydrazine* salt separates from alcohol in orange-yellow needles decomposing at 145° ; it behaves normally in freezing phenol solution. T. H. P.

Action of Nitrous Acid on α - and β -Naphthols. By JULIUS SCHMIDT (*Ber.*, 1900, 33, 3244—3246. Compare this vol., i, 89).—2 : 4-Dinitro- α -naphthol is produced when an ethereal solution of α -naphthol is saturated with the gas evolved from arsenious oxide and nitric acid; β -naphthol, when similarly treated, yields the dinitro- β -naphthol melting at 195° . G. T. M.

Addition of Aldehydoaminic Bases to Naphthols. By MARIO BETTI [with CESARE SPERONI] (*Gazzetta*, 1900, 30, ii, 301—309).—The naphthols resemble the enolic form of ethyl acetoacetate in containing the grouping $\cdot\text{CH}:\text{C}(\text{OH})\cdot$ in their molecules; and further, they give, with aldehydoaminic bases, additive compounds similar to those obtained with ethyl acetoacetate.

Benzylideneanil- β -naphthol, $\text{NHPh}\cdot\text{CHPh}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, prepared from benzylideneaniline and β -naphthol, crystallises from alcohol in aggregates of lustrous, white needles which melt at 170° and are soluble in benzene; it is readily decomposed by cold dilute acid but is stable towards alkali hydroxides. The presence of a drop of piperidine seems to greatly accelerate its formation.

m-Nitrobenzylideneanil- β -naphthol, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NHPh})\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, separates from a mixture of benzene and light petroleum as a yellowish-white, crystalline powder melting at 152° .

Benzylidene- β -naphthylamine- β -naphthol, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CHPh}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, separates from alcohol as a white, crystalline powder which melts at 175° and is slightly reddened by the action of light.

Benzylideneanil- α -naphthol, $\text{C}_{23}\text{H}_{19}\text{ON}$, is deposited by the addition of light petroleum to its benzene solution in white crystals melting at 142° to an orange-yellow liquid.

These compounds are insoluble in water and their alcoholic solutions give no coloration with aqueous ferric chloride, but in benzene solution they give a reddish-violet colour with absolute ethereal ferric chloride solution.

On mixing benzene solutions of benzylideneaniline and picric acid, yellow needles of *benzylideneaniline picrate*, $\text{C}_{19}\text{H}_{14}\text{O}_7\text{N}_4$, melting at 173° are obtained. T. H. P.

Condensation between β -Naphthol, Aldehydes, and Amines. By MARIO BETTI (*Gazzetta*, 1900, 30, ii, 310—316).—Under suitable conditions, β -naphthol condenses with an aldehyde (2 mols.) and a primary amine (1 mol.) with elimination of $2\text{H}_2\text{O}$. The substances obtained in this way crystallise well, have a high melting point, can be boiled with 25 per cent. potassium hydroxide solution without undergoing change, whilst prolonged boiling with hydrochloric acid yields the aldehyde employed; they are probably oxyazine derivatives. No condensation occurs if the β -naphthol is replaced by phenol or by diethyl malonate; secondary amines cannot replace the primary nor can acetone be used instead of an aldehyde.

β -Naphthol, benzaldehyde, and ammonia yield in almost theoretical quantity a compound, $C_{24}H_{19}ON$, crystallising from alcohol in white needles which melt at 150° and are soluble in benzene; ethereal ferric chloride gives an intense reddish-violet coloration with the benzene solution. Fusion with potassium hydroxide yields ammonia, whilst long boiling with hydrochloric acid gives benzaldehyde and a substance separating in white needles. The *acetyl* derivative of the condensation product is deposited from alcohol in lustrous, white crystals melting at 188 – 189° , and in benzene solution gives no coloration with ferric chloride.

β -Naphthol, benzaldehyde, and aniline yield a compound, $C_{30}H_{23}ON$, which is readily soluble in benzene or chloroform, and separates from amyl alcohol in rosettes of small, white needles which begin to turn yellow at 160° , become orange-coloured at 185° and melt at 200° .

From β -naphthol, furfuraldehyde, and ammonia, a compound, $C_{20}H_{15}O_3N$, is obtained, which separates from alcohol in mammillary tufts of long, white needles melting at 115° ; in benzene solution, it gives an intense violet coloration with ethereal ferric chloride.

β -Naphthol, valeraldehyde, and ammonia yield a compound, $C_{20}H_{27}ON$, crystallising from alcohol in tufts of long, lustrous white needles melting at 92° ; its benzene solution gives an intense violet coloration with ethereal ferric chloride.

T. H. P.

Etherification of Triphenylcarbinols by Alcohols. By OTTO FISCHER (*Ber.*, 1900, 33, 3356–3357).—On dissolving the malachite-green base in boiling methyl alcohol, the *methyl ether*, $C_{24}H_{28}ON_2$, separates in white leaflets which rapidly become green, and melt at 150 – 151° ; if the ether is dried rapidly over alkali, it does not subsequently become coloured. Acids, even acetic acid, remove the methoxyl group and yield salts of malachite-green. The corresponding *ethyl ether*, obtained at a temperature of 80 – 170° , forms concentrically grouped, colourless leaflets and melts at 162° ; the *benzyl ether* is obtained only at temperatures above 140 – 150° , and forms white, silky needles, which when dried over alkali, retain their colour. It softens at 195° , melts at 198° , is coloured green by acids, and is decomposed by dilute sulphuric acid at 100° into benzyl alcohol and the sulphate of the malachite-green base.

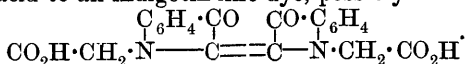
W. A. D.

Action of Nitric Acid on Tribromoguaiacol. By H. COUSIN (*Compt. rend.*, 1900, 131, 901–903).—When tribromoguaiacol, $OH \cdot C_6HBr_3 \cdot OMe$, is oxidised with nitric acid in presence of acetic acid and some alcohol, it yields a compound, $C_{19}H_4O_4Br_4$, which forms orange-red, flattened needles, melts at 186 – 188° , and is insoluble in water, but dissolves readily in organic solvents. When treated with reducing agents, it yields a colourless compound, $C_{12}H_6O_4Br_4$, which forms prismatic crystals melting at 170 – 172° . With ferric chloride, its alcoholic solution gives a green coloration which changes to violet on addition of a trace of sodium carbonate. Both compounds yield diphenyl when treated with zinc dust. The red compound is a quinone which probably has the constitution $\begin{array}{c} OH \cdot C_6HBr_2 \cdot O \\ OH \cdot C_6HBr_2 \cdot O \end{array}$, whilst

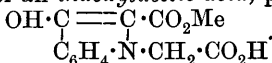
the colourless compound is the corresponding quinol. The action of nitric acid on tribromoguaiacol is similar to, but not identical with, its action on trichloroguaiacol (Abstr., 1900, i, 487). C. H. B.

Anilodiacetic-*o*-carboxylic Acid. By DANIEL VORLÄNDER and E. MUMME (*Ber.*, 1900, 33, 3182—3183).—*Anilodiacetic-*o*-carboxylic acid* (*diaceticanthranilic acid*), $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, is obtained when anthranilic acid and excess of chloroacetic acid interact in neutral or alkaline solution. It crystallises from hot water in colourless tablets or leaflets and melts and decomposes at 212° . Its conductivity shows it to be powerfully acidic, but it cannot be titrated as a tribasic acid. It is not acted on by nitrous acid and its alcoholic solution is not coloured by ferric chloride. Unlike phenylglycinecarboxylic acid, it is readily esterified and with alcohol and sulphuric acid is converted into its *trimethyl ester*, $\text{C}_{11}\text{H}_8\text{O}_6\text{NMe}_3$, melting at 62° .

When the acid is heated with alkali hydroxides, it condenses to an indoxyl derivative which is oxidised by ferric chloride and strong hydrochloric acid to an indigotin-like dye, possibly



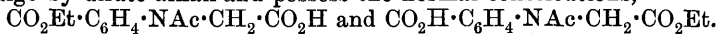
The trimethyl ester, on treatment with sodium ethoxide, is converted into the *methyl ester* of an *indoxylacetic acid*, possibly



This is a well-crystallised substance and melts at 163° .

A. L.

Esters of Acylphenylglycine-*o*-carboxylic Acids. By DANIEL VORLÄNDER and W. MEUSEL (*Ber.*, 1900, 33, 3183—3185).—It has been shown by Vorländer and Weissbrenner (Abstr., 1900, i, 295) that the acetyl derivatives of phenylglycinecarboxylic acid are readily converted by acids or alkalis into indigotin. It was presumed that these esters might be derivatives of the type $\text{C}_6\text{H}_4\cdot\overset{\text{C}(\text{OH})(\text{OR})}{\underset{\text{N}(\text{CO}\cdot\text{R})}{\text{C}}}\text{CH}\cdot\text{CO}_2\text{R}$, the conversion of which into indigotin derivatives would be readily understood. Diethylacetylphenylglycinecarboxylate may be prepared by the following different processes: 1, esterification of acetylphenylglycinecarboxylic acid; 2, acetylation of the esters of phenylglycinecarboxylic acid; and 3, action of ethyl iodide on silver acetylphenylglycinecarboxylate. Moreover, the isomeric monoethyl esters, $\text{C}_{13}\text{H}_{15}\text{O}_5\text{N}$, of acetylphenylglycinecarboxylic acid have been prepared; that obtained by partial hydrolysis of the diethyl ester melts at $130\text{--}132^\circ$, and that by partial esterification of the acid at $86\text{--}87^\circ$. These are not converted into indigo by dilute alkali and possess the normal constitutions,



The authors have finally proved that it is possible to detect indoxyl derivatives by means of warm 60 per cent. sulphuric acid, which converts them into indigotinsulphonic acids.

The authors draw the conclusion that the diethyl esters referred to are true derivatives of acetylphenylglycinecarboxylic acid and that their conversion into indigotin is preceded by intramolecular change into indoxyl derivatives.

A. L.

Action of Air and Water on β -Benzylhydroxylamine. By EUGEN BAMBERGER and BOGDAN SZOLAYSKI (*Ber.*, 1900, 33, 3193—3201. Compare Abstr., 1900, i, 531).—When pure air is passed through β -benzylhydroxylamine suspended in water for several months, it is converted into a dense, viscid oil, which finally becomes semi-solid. The product contains benzaldoxime, benzaldehyde, and benzoic acid, benzylisobenzaldioxime, $O\left\langle \begin{smallmatrix} CHPh \\ N \cdot CH_2Ph \end{smallmatrix} \right\rangle$, benzaldoxime anhydride, $C_{14}H_{12}ON_2$, a neutral substance melting at $212-213^\circ$, benzylidenebenzhydrazide, $CHPh:N \cdot NH \cdot CPh$, dibenzoylhydrazine, $C_{14}H_{12}O_2N_2$. Bisnitrosobenzyl and azoxybenzyl could not be detected. As in the case of the oxidation of arylhydroxylamines, hydrogen peroxide is produced in considerable quantities. The neutral substance above mentioned crystallises in white, silky, felted needles, is very sparingly soluble in alcohol, and is indifferent towards bases and acids; its nature has not yet been ascertained. A. L.

Nitrosulphosalicylic Acids. By ROBERT HIRSCH (*Ber.*, 1900, 33, 3238—3241).—Sulphosalicylic acid (Mendius, *Annalen*, 1857, 103, 45), prepared by the action of sulphuric acid on salicylic acid at 100° , can be salted out from its solution, and can be crystallised from a concentrated salt solution or from a little hot water. Contrary to Remsen's statement (Abstr., 1874, 1167; 1876, i, 594), the acid appears to be homogeneous, and only one potassium salt could be isolated. The nitration of salicylic acid (Hübner, Abstr., 1876, i, 593; 1879, 380) can be carried out smoothly by dissolving in sulphuric acid and adding a mixture of nitric and sulphuric acids until no marked rise of temperature occurs on mixing, the temperature being kept below 10° . A nitrosulphosalicylic acid can be prepared by nitrating sulphosalicylic acid at $30-40^\circ$ by the method just described. The barium salt, $OH \cdot C_6H_2(NO_2) \left\langle \begin{smallmatrix} CO_2 \\ SO_3 \end{smallmatrix} \right\rangle Ba$, crystallises from hot water in yellowish-red needles, and is almost insoluble in cold water. T. M. L.

Hydroxyphenylcinnamic Acid. By MARUSSIA BAKUNIN (*Gazzetta*, 1900, 30, ii, 370—377).—The hydroxyphenylcinnamic acid melting at 120° prepared by Vandevelde (Abstr., 1898, i, 670) by the interaction of sodium hydroxyphenylacetate, benzaldehyde, and acetic anhydride is a mixture of cinnamic acid and the hydroxyphenylcinnamic acid melting at 181° obtained by Ogialoro (Abstr., 1881, 276). The phenyl ester melts at 107° , and not, as stated by Vandevelde, at 74° , which is the melting point of phenyl cinnamate.

T. H. P.

Addition of Ketomethane Derivatives to Unsaturated Compounds. By DANIEL VORLÄNDER (*Ber.*, 1900, 33, 3185—3187).—It is often observed that ethyl sodiomalonate will unite with $\alpha\beta$ -unsaturated ketones when benzene or ether is used as the diluent, but not if alcohol is used. The explanation of this appears to be that the reaction is a reversible one, and that the reverse change is slower in the non-hydroxylic solvents.

Thus, whilst ethyl pulegonemalonate may be prepared by heating

pulegone with ethyl sodiomalonate dissolved in benzene or ether, it is broken up into these constituents when heated with an alcoholic solution of sodium ethoxide. In a similar manner, ethyl benzylidenebis-benzoylacetate is converted by alcoholic sodium ethoxide into ethyl benzoylacetate and ethyl benzylidenebenzoylacetate (compare also Dieckmann, Abstr., 1900, i, 623). A. L.

A Saturated Dicyclic Dicarboxylic Acid. By WILHELM BRAREN and EDUARD BUCHNER (*Ber.*, 1900, 33, 3453—3456).—*Ethyl Δ'-tetrahydrobenzoate* prepared from the corresponding acid (Aschan Abstr., 1891, 1481; 1893, i, 33) is an oil boiling at 206—208°, which, when heated with ethyl diazoacetate at 110—120° for 16—24 hours or until all the diazoacetate has disappeared, yields *ethyl 1:2-norcarandicarboxylate*, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Et}) \end{array} \text{---} \text{CH} \cdot \text{CO}_2\text{Et}$; this, after purification by distillation in steam, forms an oil boiling at 159—160° under 18 mm pressure; on hydrolysis with alcoholic potash, it yields *cis-1:2-norcarandicarboxylic acid*, $\text{C}_7\text{H}_{10}(\text{CO}_2\text{H})_2$, together with an oily mass; the *cis*-acid melts at 152—153°, is readily soluble in water, alcohol or ether, and is not acted on by cold permanganate in alkaline solution. When boiled for $1\frac{1}{2}$ hours with acetyl chloride, it yields the *anhydride*, $\text{C}_7\text{H}_{10} \cdot \text{C}_2\text{O}_3$, which crystallises from carbon disulphide in colourless plates melting at 86—87°; when this is dissolved in sodium hydroxide solution and then acidified, it yields the original acid, and hence follows the *cis*-configuration of the latter. J. J. S.

Euxanthic Acid. By CARL GRAEBE (*Ber.*, 1900, 33, 3360—3362).—Although the potassium and sodium salts of euxanthic acid are of the type $\text{C}_{19}\text{H}_{17}\text{O}_{11}\text{M}$, the *silver* salt, precipitated from the potassium salt by silver nitrate, has the composition $\text{C}_{19}\text{H}_{15}\text{O}_{10}\text{Ag}$, derived from an anhydride of the acid; the *methyl* ester melting at 212°, and the *ethyl* ester, melting at 198°, prepared from the silver salt are of a similar type, $\text{C}_{19}\text{H}_{15}\text{O}_{10} \cdot \text{R}$. These esters, but not the free acid, combine directly with iodine (apparently 2 atoms at most) to form gelatinous, insoluble blue substances. With acetic anhydride, the esters yield colourless *acetyl* derivatives, derived not from the esters themselves, but from the anhydride, $\text{C}_{19}\text{H}_{16}\text{O}_{10}$; their composition remains to be determined. With benzoyl chloride, analogous substances are formed, the ultimate product being the compound $\text{C}_{19}\text{H}_{11}\text{O}_{10}\text{Bz}_5$. W. A. D.

Lichens and their Characteristic Constituents. By OSWALD HESSE (*J. pr. Chem.*, 1900, [ii], 62, 321—363. Compare Abstr., 1898, i, 531, 679; 1899, i, 381).—Specimens of usnic acid obtained from *Usnea ceratina*, *Cladonia rangifera* var. *silvatica*, *Parmelia caperata* and *Placodium saxicolum* var. *vulgare* gave $[\alpha]_D + 494.1^\circ$, $+ 494.6^\circ$, $+ 492.2^\circ$, and $+ 492.7^\circ$ respectively, whilst that from *Cetraria pinastri* gave $[\alpha]_D - 494.1^\circ$. When either *d*- or *l*-usnic acid is melted, it is instantly converted into the inactive modification. The *d*-acid melts at 195—197°, the *l*-acid at 197°, and the inactive form at 192—193°. The *potassium* salts of the *d*- and *l*-acids crystallise from water with $3\text{H}_2\text{O}$, and from alcohol with $1\text{H}_2\text{O}$. The inactive modifications

obtained by fusion of the *d*- and *l*-acid respectively and that crystallised from a mixture of the two active forms are not absolutely identical, since the potassium salt crystallises in a different form in each case; the sodium salt, however, crystallises only in one form (compare Widman, Abstr., 1900, i, 235).

Ebullioscopic determination of the molecular weight of the substance obtained by the action of acetic anhydride on *d*-usnic acid (Hesse, Abstr., 1895, i, 298) gave 338—339, whilst a substance of the formula $(C_{18}H_{15}O_6)_2O$ requires 670; the author concludes that the supposed anhydride is a mixture of the lactone, $C_{18}H_{14}O_6$, and the *d*-acid.

A further examination of *Candelaria concolor* has shown that the 'dipulvic acid' previously described consists of pulvic anhydride together with a smaller quantity of calycin (compare Zopf, Abstr., 1899, i, 716). *Candelaria vitellina* obtained from four different sources furnished a substance composed of calycin and pulvic anhydride in varying proportions. *Sticta aurata* yields 'stictaurin,' $C_{18}H_{12}O_5$, which has the properties attributed to it by Zopf (*loc. cit.*). *Sticta Desfontainii a-munda* contains a substance melting at 232° which, when boiled with alcohol, furnishes calycin and ethylpulvic acid. If calycin (1 mol.) and pulvic anhydride (2 mols.) are dissolved in hot glacial acetic acid, a substance, $C_{18}H_{12}O_5 \cdot (C_{18}H_{10}O_4)_2$, separates which corresponds in every way with that obtained from *Sticta aurata* and crystallised from the same solvent; in one case, a substance, $C_{18}H_{12}O_5$, was produced resembling that obtained directly from *Sticta aurata* by extraction with ether. From a solution of calycin and pulvic anhydride in molecular proportion, a substance is obtained in brick-red needles which melts at 216—217°, and agrees in its characters with that yielded by *Candelaria vitellina*. If, however, more than 1 mol. of calycin is mixed with 1 mol. of pulvic anhydride, the excess of the former crystallises independently. The author concludes that the colouring matter of these lichens is not a definite single substance, but a mixture of calycin and pulvic anhydride in varying proportions, and that the calycin protects the anhydride from alteration.

Calycium chlorellum (*C. chlorinum*), yields vulpic acid and traces of lepraric.

Calycium flavum contains chrysocetraric acid and calycin.

When *Acolium tigillare* is extracted with ether, and the ethereal solution shaken with aqueous potassium hydrogen carbonate, the potassium salt of acolic acid separates, whilst rhizocarpic acid remains in solution. *Acolic acid* crystallises in small, white needles, melts and evolves gas at 176°, and is fairly soluble in alcohol, benzene, or chloroform when hot, but only sparingly at the ordinary temperature. The ammonium, potassium, and barium salts are described.

The investigation of the constituents of *Cetraria islandica* has been continued; the sample examined consisted chiefly of var. *vulgaris* and *platyna*. Lichenostearic acid is found to be a mixture of three acids, which the author terms α -, β -, and γ -lichenostearic acid.

α -Lichenostearic acid, $C_{18}H_{30}O_5$, is a monobasic acid which crystallises in prisms or plates, melts at 122—123°, gives $[\alpha]_D + 27.9^\circ$, and is soluble in benzene, chloroform, or hot glacial acetic acid; its potassium, sodium, ammonium, barium, and silver salts are described. The

methyl ester, obtained by the action of methyl iodide on the potassium salt, crystallises in colourless needles, melts at 50.5° , and dissolves readily in alcohol or ether. The *ethyl* ester forms long, radiating crystals, melts at $29-30^{\circ}$, and is easily soluble in ether or alcohol. When α -lichenostearic acid is heated with aqueous barium hydroxide, it loses carbon dioxide and is converted into *lichestrone*, $C_{17}H_{30}O_3$, the lactone of lichestronic acid; lichestrone crystallises in white, lustrous plates, melts at $83-84^{\circ}$, is optically inactive, and dissolves readily in alcohol, ether, acetone, chloroform, benzene, or glacial acetic acid. It dissolves slowly in solution of potassium hydrogen carbonate, with formation of lichestronic acid; this change takes place more rapidly if potassium carbonate or hydroxide is employed.

Lichestronic acid, $C_{17}H_{32}O_4$, is monobasic; it crystallises from dilute acetic acid in prisms or plates, melts at 80° , is optically inactive, and dissolves very easily in alcohol, ether, benzene, or chloroform; its *barium* salt was prepared and analysed.

β -*Lichenostearic acid*, $C_{18}H_{30}O_5$, crystallises from acetic acid in leaflets, melts at 121° , gives $[\alpha]_D + 27.9^{\circ}$, and by the action of baryta is converted into lichestrone; its *sodium*, *ammonium*, and *barium* salts are described. α - and β -Lichenostearic acids are readily distinguished by means of their ammonium salts; the ammonium salt of the former acid is sparingly soluble in cold water, whilst that of the latter acid is very easily soluble, and is precipitated in a gelatinous form on addition of excess of ammonium chloride.

γ -*Lichenostearic acid*, $C_{18}H_{30}O_5$, or $C_{19}H_{32}O_5$, melts at $121-122^{\circ}$, and gives $[\alpha]_D + 16.0^{\circ}$; when its solution in benzene is heated, it is to a great extent polymerised. The *ammonium* salt is readily soluble in water; the *barium* salt is insoluble in water, whilst that of the β -acid is very easily soluble.

Paralichenostearic acid, $C_{20}H_{34}O_5$ (Abstr., 1899, i, 386), melts at 182° .

The foregoing acids are accompanied by smaller quantities of two other acids. The first of these has the composition $C_{18}H_{30}O_5$; when crystallised from alcohol, it melts at 140° , but if crystallised from glacial acetic acid, melts at 152° ; its *barium* salt was prepared and analysed. The second acid is *dilichenostearic acid*, $C_{36}H_{60}O_{10}$, which melts at 272° , gives $[\alpha]_D + 15.2^{\circ}$, and is easily soluble in ether, amyl alcohol, or hot chloroform, and sparingly in benzene, light petroleum, or hot alcohol; determination of the molecular weight by the boiling point method gave 659 ($C_{36}H_{60}O_{11}$ requires 652); its *sodium*, *ammonium*, and *barium* salts are described.

The author was unable to detect any phytosterol, or similar substance, among the constituents of *Cetraria islandica*. The lichenostearic acid described by Sinnhold (Abstr., 1899, i, 13), is probably the α -acid, whilst his lichenosterylic acid appears to be lichestrone.

E. G.

Compounds from Lichens. VII. By WILHELM ZOPF (*Annalen*, 1900, 313, 317-344. Compare Abstr., 1899, i, 716).—*Lepraria latebrarum* (Ach.) yields roccellaric acid, atranoric acid, and leprarin, which melts at 155° ; methyl, ethyl, and propyl alcohols, under the influence of hydrochloric acid, convert leprarin into *leprarinin*, melting at 135°

lepraridin, melting at 120—121°, and *lepralin*, melting at 100°, respectively. *Gyrophora vellea* and *G. spodochoa* (Ehrh.) var. *depressa* contain gyrophoric acid, which in the former lichen is associated with *gyrophorin*; this crystallises from alcohol in minute, rhombic plates, and melts, evolving gas, at 189°. Usnic acid has been identified in *Ramalina thrausta* (Ach.), *Alectoria sarmentosa* (Ach.), *Cladonia deformis* (L.), *C. cyanipes* (Sommerfelt), and *Parmelia incurva* (Pers.). *Lecanora epanora* (Ach.) contains zeorin and *epanorin*, which crystallises from warm ether in lemon-yellow needles, and melts at 131—132°. *Parmelia Borreri* (Turn.) yields lecanoric acid, and *P. sorediata* (Ach.) contains diffusin; the greenish-yellow colour of *Rhizocarpon viridiatrum* (Flörke) is due to rhizocarpic acid.

The author has isolated salazinic acid and picrolichenin from *Pertusaria amara* (compare Hesse, Abstr., 1899, i, 383), and corrects his former statement to the effect that *Physcia caesia* (Hoffm.) contains hæmatomic acid. The compound in *Evernia furfuracea* (L.), at first thought to be erythrin, is now recognised as a new substance, *olivetic acid*, $C_{27}H_{36}O_8$, which crystallises from 55 per cent. alcohol in long, silky needles, and melts at 141—142°; when heated with methyl alcohol in sealed tubes at 150°, it yields *olivetricinic acid*, which sinters at 65°, and melts at 88°. M. O. F.

Disulphones. V. Acetophenone and Benzophenone Disulphones. By THEODOR POSNER (*Ber.*, 1900, 33, 3165—3168. Compare this vol., i, 14).—According to Baumann (*Ber.*, 1886, 19, 2803) aromatic and aromatic-aliphatic ketones do not yield disulphones by conversion into mercaptols and oxidation; the author has, however, succeeded in obtaining disulphones from acetophenone and benzophenone. *aa-Diethylthiol- α -phenylethane* (*acetophenonemercaptol*), $CMePh(SET)_2$, is readily formed when hydrogen chloride is passed into an acetic acid solution of acetophenone and ethyl mercaptan. It is an oily compound, and on oxidation yields *aa-diethylsulphone- α -phenylethane* (*acetophenonedisulphone*) melting at 119—120° (corr.); this compound is identical with that described by Fromm (*Annalen*, 1889, 253, 135) as melting at 100—101°.

Diethylsulphonediphenylmethane (*benzophenonedisulphone*),
 $CPh_2(SO_2Et)_2$,

forms small, nodular crystals melting at 136—137° (corr.). J. J. S.

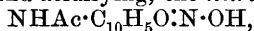
Action of Nitrous Acid on Benzoquinone. By JULIUS SCHMIDT (*Ber.*, 1900, 33, 3246—3250).—*Nitroanilic acid benzoquinone*, $OH \cdot C_6(NO_2)_2 \cdot O_2 \cdot O_2 \cdot C_6H_4$, obtained by saturating a cooled ethereal solution of benzoquinone with the fumes evolved from nitric acid and arsenious oxide, crystallises in lustrous yellow prisms, and decomposes at 160°, it is readily soluble in acetone, ethyl acetate, or the alcohols, and dissolves only sparingly in chloroform, benzene, or toluene. An intense bluish-red coloration is developed on treating its alcoholic solution with ferric chloride. When dissolved in water, it dissociates into benzoquinone and nitroanilic acid; alkalis decompose it, yielding the quinone and an alkali nitroanilate, sodium ethoxide in alcoholic solution giving rise to the sodium salt.

A mixture of benzoquinone and liquid nitrogen trioxide after re-

maining for 24 hours in a sealed tube at 12° , exploded with sufficient violence to completely shatter the wrought-iron sheath surrounding the experimental tube.

G. T. M.

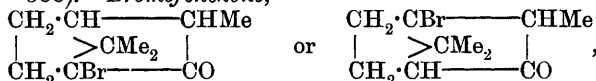
5-Acetylamino-1:2-naphthaquinone and the *iso*Rosindulines obtained therefrom. By FRIEDRICH KEHRMANN and A. DENK (*Ber.*, 1900, 33, 3295—3300).—5-Amino-2-naphthol interacts with acetic anhydride at the ordinary temperature to form 5-acetylamino-2-naphthol, which crystallises from alcohol in greyish needles and melts at $213\text{--}214^\circ$. On dissolving it in dilute aqueous sodium hydroxide, adding sodium nitrite, and acidifying, the nitroso-derivative,



is obtained; this crystallises from water, gives a bright green sodium salt, and on reduction with stannous chloride in 20 per cent. hydrochloric acid yields 5-acetylamino-1-amino-2-naphthol, which is readily oxidised by potassium dichromate and sulphuric acid to 5-acetylamino-1:2-naphthaquinone. This crystallises from chloroform in vermilion needles, melts at $150\text{--}160^\circ$, is easily soluble in water, and condenses at the ordinary temperature with *o*-aminodiphenylamine to form principally *isorosinduline* No. 9 (Kehrmann and Steiner, this vol., i, 101) along with a small quantity of the isomeride No. 12 (*ibid.*, 100).

W. A. D.

Bromofenchone. By LUIGI BALBIANO (*Gazzetta*, 1900, 30, ii, 382—388).—*Bromofenchone*,



obtained in small yield by gradually adding the theoretical quantity of bromine to fenchone heated at $140\text{--}150^\circ$, is a pale yellow, oily liquid which has an aromatic, terpene-like odour and dissolves in most organic solvents; it boils undecomposed at 120° under 14 mm., and at 107° under 2 mm. pressure, has a sp. gr. 1.328 at $15^\circ/15^\circ$ and $[\alpha]_D - 6.8^\circ$ at 9° . On reduction in alcoholic solution with zinc and sulphuric acid, it yields fenchone, but when oxidised with various oxidising reagents no definite products other than carbon dioxide, oxalic acid, and resinous acids could be obtained.

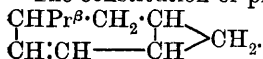
T. H. P.

Terpenes and Ethereal Oils. By OTTO WALLACH (*Annalen*, 1900, 313, 345—370. Compare *Abstr.*, 1896, i, 101).—[With H. and E. LAUFFER.]—When purified phellandrene nitrite is treated with ammonia of sp. gr. 0.93, it is very slowly dissolved, nitrous oxide being evolved; a white solid is produced which yields nitrophellandrene when heated with water, acids, or alkalis, and this disagreement with the observations of Pesci (*Abstr.*, 1886, 1038) is due to the fact that the material employed by that investigator was not purified sufficiently. Nitrophellandrene is also produced when phellandrene nitrite is added to acetic chloride.

Oxidation with nitric acid converts phellandrene nitrite into a neutral compound containing nitrogen, along with terephthalic and isopropylsuccinic acids, and an acid isomeric with the last-named substance. The compound, $\text{C}_7\text{H}_{10}\text{O}_4\text{N}_2$, melts at $88\text{--}89^\circ$, and gives Liebermann's reaction for nitroso-compounds; the acid, $\text{C}_7\text{H}_{12}\text{O}_4$, melts

at 85—88°. *iso*Propylsuccinic acid is also produced when phellandrene nitrite is oxidised with potassium permanganate.

The constitution of phellandrene is best represented by the formula



[With H. LAUFFER.]—The base, $\text{C}_{10}\text{H}_{17} \cdot \text{NH}_2$, prepared by reducing terpinene nitrosite with sodium in alcohol, boils at 209—210°, has a sp. gr. 0.8725, and n_D 1.4717 at 20°; the carbamide derivative melts at 171°. Oxidising the corresponding alcohol converts it into the ketone, of which the *oxime* melts at 96—98°. *p*-Cymene is the non-basic reduction product of terpinene nitrosite.

[With ALFRED SCHÄFER.]—When α -pinonic acid is prepared by oxidising oil of turpentine, a peculiar, camphor-like odour is noticeable on evaporating the liquid; this is due to nopinone, the ketone obtained by oxidising nopic acid.

[With WILHELM ROJAHN.]—*Pinocamphylamine*, $\text{C}_{10}\text{H}_{17} \cdot \text{NH}_2$, prepared by reducing pinocamphoneoxime (Abstr., 1898, i, 486) with sodium in alcohol, is a liquid which rapidly absorbs carbon dioxide; the *carbamide* and *acetyl* derivatives melt at 204° and 120° respectively. Pinocamphonitrile (*loc. cit.*) boils at 224—226°, and is hydrolysed to *pinocampholenic acid*, $\text{C}_{10}\text{H}_{16}\text{O}_2$, which yields the amide melting at 116°.

Whilst nitrosopinene yields a mixture of pinylamine and pinocamphone on reduction, the additive compound with bromine is converted into dihydrocarvone and dihydrocarvylamine. M. O. F.

Camphene. By FRIEDRICH W. SEMMLER (*Ber.*, 1900, 33, 3420—3432).—Camphene is never oxidised to camphoric acid, and probably contains a nucleus different from those of pinene and of

pinene hydrochloride. The formula $\text{CMe} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CMe}_2 \\ \text{C}(\text{CH}_2) \end{array} \text{CH}$ is suggested for camphene.

Pinene dibromide is reduced to a dihydrocamphene identical with that from pinene hydrochloride; it therefore contains the same nucleus as the latter, and is the product of an isomeric change similar to that which takes place in the action of hydrogen chloride on pinene.

Bromocamphene, for which the formula $\text{CMe} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CMe}_2 \\ \text{C}(\text{CH}_2) \end{array} \text{CBr}$ is

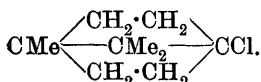
suggested, is reduced by sodium and alcohol to camphene, and therefore contains the camphene nucleus unchanged. Camphene dibromide is probably formed by the addition of hydrogen bromide to the bromocamphene which is the first product of the action, and is reconverted into bromocamphene by distilling with quinoline. It is not, however, readily acted on by alcoholic potash, and is reduced by sodium and alcohol to a dihydrocamphene identical with that from pinene hydrochloride; it is therefore suggested that it has the same nucleus as the

latter, and the formula $\text{CMe} \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \text{CMe}_2 \\ \text{CHBr} \cdot \text{CH}_2 \end{array} \text{CBr}$ is suggested; the

conversion of bromocamphene into camphenedibromide would then involve the conversion of a four-membered into a five-membered ring, as in the conversion of pinene into the hydrochloride.

Camphene hydrobromide, $C_{10}H_{16}HBr$, separates from alcohol in well-formed crystals and melts at 133° ; it is reconverted into camphene by alcoholic alkalis, and also when attempts are made to reduce it with sodium and alcohol. The hydrochloride loses hydrogen chloride less readily, and gives a mixture of camphene and dihydrocamphene identical with that from pinene hydrochloride; it is suggested that the

hydrochloride is perhaps a mixture of $CMe \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{---} CMe_2 \text{---} \\ \text{---} CMeCl \text{---} \end{array} CH$ and



Camphene alcoholate, $C_{10}H_{17} \cdot OEt$, prepared by boiling a mixture of camphene, alcohol, and sulphuric acid, is an oil which boils at about 200° , has n_D 1.4589, a sp. gr. 0.895, and is identical with *isoborneol ethyl ether* (Bertram and Walbaum, Abstr., 1894, i, 204); this reaction does not take place with other terpenes, although nopinene and sabinene give small yields of an ether. *isoBorneol* gives a small yield of camphor when oxidised with dichromate and sulphuric acid; it

may be a camphane derivative, $CMe \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{---} CMe_2 \text{---} \\ \text{---} CH_2 \cdot CH_2 \end{array} C \cdot OH$, or a cam-

phene derivative, $CMe \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{---} CMe_2 \text{---} \\ \text{---} CMe(OH) \end{array} CH$, or a mixture of these.

T. M. L.

The Resin-Balsam of *Picea Vulgaris*, Link (*Jura Turpentine*). By ALEXANDER TSCHIRCH and ED. BRÜNING (*Arch. Pharm.*, 1900, 238, 616—630).—This turpentine was examined by the methods already described (Abstr., 1900, i, 678, &c.). From a solution of it in ether, 1 per cent. aqueous ammonium carbonate extracts *piceapimaric acid*, $C_{13}H_{20}O_2$, an amorphous substance, which neutralises 1KOH both in the cold and on boiling. After this treatment, 1 per cent. aqueous sodium carbonate extracts a mixture of acids, from the solution of which in methyl alcohol *piceapimaric acid*, $C_{20}H_{30}O_2$, crystallises; this melts at 144 — 145° , and neutralises 1KOH both in the cold and on boiling; *mono-potassium*, *calcium*, *lead*, and *silver* salts were prepared. From the mother liquors of this acid, two isomeric *piceapimarolic acids*, $C_{25}H_{44}O_2$, separate; these are amorphous, and can be separated with alcoholic lead acetate, which precipitates the lead salt of the α -acid, but not that of the β -acid; the acids melt at 90 — 95° and 88 — 94° respectively; both neutralise 1KOH as well in the cold as on boiling. These resinolic acids all give the colour reactions of the cholesterol.

After removal of the acids and further washing with dilute aqueous potassium hydroxide, the ether was distilled off, and the residue distilled with steam; an *etheral oil* came over, smelling like turpentine. There remained behind a substance of indifferent character, *juvioresen*, $C_{21}H_{36}O$.

An *alkaloid* can be extracted from the turpentine with hot water. The turpentine also contains a *colouring matter*, and it yields formic, acetic, and succinic acids when distilled; no methoxyl is present.

In 100 parts of the drug there are contained: piceapimaric acid, 2—3; piceapimaric acid, 1·5—2; α - and β -piceapimarolic acids (the former in larger amount), 48—50; ethereal oil, 32—33; juroresen, 10—12; succinic acid, colouring matter, alkaloid, water and impurities, 1—2 parts. C. F. B.

Synthesis of Luteolin. By STANISLAUS VON KOSTANECKI, A. RÓŻYCKI and JOSEF TAMBOR (*Ber.*, 1900, 33, 3410—3417).—When 2:4:6-trimethoxyacetophenone and ethyl piperonylate dissolved in xylene are heated with sodium for 10—12 hours at 120°, condensation ensues with the formation of 2:4:6-trimethoxybenzoyl-3':4'-methylene-dioxyacetophenone, $C_6H_2(OMe)_3 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_3O_2 \cdot CH_2$, which crystallises in small, yellow needles, melts at 115° and when warmed with hydriodic acid yields 5:7-dimethoxy-3':4'-methylenedioxyflavone, which crystallises in clusters of silky, white needles, melts at 232°, and forms fluorescent solutions.

As this compound is not easily converted into tetrahydroxyflavone, 2:4:6:3':4'-pentamethoxybenzoylacetophenone was prepared by the condensation of 2:4:6-trimethoxyacetophenone with ethyl veratrate; this is precipitated by carbon dioxide from its solution in sodium hydroxide as a white, curdy precipitate and, when treated with strong hydriodic acid, yields luteolin. R. H. P.

Hydrolysis of Solanin. By FERDINAND SCHULZ (*Zeit. Zuck.-Ind. Böhm.*, 1900, 25, 89—94).—On hydrolysis, solanin yields about 47·52 per cent. of its weight of solanidin and 42·41 per cent. of sugar (calculated as dextrose), the latter being a mixture of dextrose with a methylpentose, probably rhamnose. T. H. P.

Oxidation of Aloin with Potassium Persulphate and with Caro's Acid. By EUGEN SEEL (*Ber.*, 1900, 33, 3212—3214).—By the action of an excess of potassium persulphate on aloin, a red substance is produced, perhaps identical with Schaer's 'aloin red' (*Abstr.*, 1900, i, 512). Caro's reagent gives a tetrahydroxymethylanthraquinone, $C_{15}H_{10}O_6$, which is perhaps identical with Oesterle's 'alochrysin' (*Abstr.*, 1899, i, 538). T. M. L.

Crystalline Compounds in Galanga Root. By GIUSEPPE TESTONI (*Gazzetta*, 1900, 30, ii, 327—339).—Alpinin, $C_{17}H_{12}O_6$, which Jahns (*Abstr.*, 1882, 866) isolated, together with campheride and galangin, from galanga root (*Alpinia officinarum*), is shown by the author to be a mixture of the two last-named compounds.

The methyl derivative of galangin, $C_{16}H_{12}O_5$, is also present in galanga root and crystallises from methyl alcohol in pale yellow, square plates melting at about 300°. It dissolves in concentrated sulphuric acid, forming a deep yellow liquid which in a short time assumes a green fluorescence; it is also soluble in concentrated potassium hydroxide solution, giving an intense yellow colour, whilst with sodium hydroxide the corresponding salt is precipitated in minute yellow needles. Its diacetyl compound, $C_{20}H_{16}O_7$, separates from alco-

hol in faintly yellow leaflets melting at $175-176^{\circ}$ and forms a *di-bromide*, $C_{20}H_{16}O_7Br_2$, crystallising from acetic acid in yellow needles melting at 202° . The methyl derivative is transformed into galangin by hydriodic acid.

Jahns (*loc. cit.*) and Gordin (*Diss.*) prepared diacetyl- and dibenzoyl-derivatives of campheride, but the author has obtained trisubstituted derivatives, thus confirming the constitution given by von Kostanecki (*Abstr.*, 1896, i, 44). *Triacetylcampheride*, $C_{16}H_9O_6Ac_3$, separates from alcohol in almost white needles melting at $193-194^{\circ}$ and the *tribenzoyl* compound crystallises from acetic acid in white, mammillary masses melting at $177-178^{\circ}$.

On methylating campheride with methyl iodide and alcoholic potash, it yields mainly a *trimethyl* derivative, $C_{19}H_{20}O_6$, separating from methyl alcohol in square or rectangular yellow plates melting at 178° , whilst ethylation yields a *diethyl* derivative, $C_{20}H_{20}O_6$, crystallising from methyl alcohol in slender, yellow needles melting at $137-139^{\circ}$ and a *triethyl* compound, $C_{22}H_{24}O_6$, separating from light petroleum in long, yellow needles melting at $125-126^{\circ}$. In these trisubstituted derivatives, one of the alkyl groups enters the nucleus of the molecule and is not present in the form of a methoxy- or ethoxy-residue.

T. H. P.

Tiliadin, a Constituent of the Bark of Lime Trees. By WALTER BRAEUTIGAM (*Arch. Pharm.*, 1900, 238, 555-567).—When the bark of the lime tree is extracted with ether, the extract evaporated, and the residue washed thoroughly with 90 per cent. alcohol, the alcohol extracts a little vanillin. If the residue is boiled with 5 per cent. aqueous potash and then dissolved in ether, the solution deposits crystalline plates as it evaporates; this substance, *tiliadin*, $C_{21}H_{32}O_2$, melts at $228-229^{\circ}$, volatilises when heated cautiously, and is dextrorotatory in chloroform solution. In many of its reactions it resembles the cholesterol, but in others it differs from them; it has not the properties of a glucoside. It does not lose water of crystallisation when heated at 125° , nor will it form acetyl or benzoyl derivatives. Strong hydrochloric acid is without effect on it, even at 160° . Boiling with aqueous alkali hydroxides is without effect; on the other hand, alcoholic potash at 150° converts it into a substance, $C_{13}H_{18}O$, which crystallises in needles, begins to melt at $179-180^{\circ}$, and volatilises when heated cautiously. Fusion with potassium hydroxide converts tiliadin into resinous products, but oxalic acid is not formed. Boiling with nitric acid has no effect, but at 160° a resinous product is obtained. Potassium permanganate does not oxidise it in cold acetic acid solution, but it does on boiling, and so does chromic acid; the product is a resinous substance, with the composition $C_{21}H_{32}O_4$. When treated with chlorine or bromine in chloroform solution, tiliadin yields products containing chlorine and bromine; with iodine, no similar product could be obtained.

On the west side of the tree, the bark frequently has a green coating of an alga, *Pleurococcus vulgaris*; from this a substance crystallising in needles was obtained; these crystallise out along with the

plates of tiliadin in the preparation of the latter, if the bark has not been freed from the green coating. C. F. B.

Blue Chlorophyllin. By M. TSVETT (*Compt. rend.*, 1900, 131, 842—844).—The blue chlorophyllin was isolated from the plants by a method which is described in detail. It was obtained in a micro-crystalline state, the crystals having a black colour and a bluish lustre. The absorption spectrum of its solution consists of six bands, the fourth band being situated near the Fraunhofer line E, and the fifth commences at the line F. H. R. LE S.

Composition of the Orange Pigment of Uraster Rubens. By ARTHUR BOWER GRIFFITHS and F. W. WARREN (*Bull. Soc. Chim.*, 1900, [iii], 23, 874—875).—The orange pigment extracted from the skin of *Uraster rubens* has the composition $C_{16}H_{18}O_2N_4$; its solutions do not show characteristic absorption bands. N. L.

Syntheses of Coumaranone (Ketocoumaran) and its Homologues from Phenoxyacetic Acid. By RICHARD STOERMER and F. BARTSCH (*Ber.*, 1900, 33, 3175—3181. Compare Abstr., 1899, i, 675).—Coumaranone is most easily obtained by the dehydration of phenoxyacetic acid suspended in benzene with phosphoric oxide, and is separated from the unaltered acid by distillation with steam; when pure, it is quite stable and has a pleasant odour of hyacinths. It sublimes at the ordinary temperature in long, slender needles and melts at 101—102°. The *semicarbazone*, $C_9H_9O_2N_3$, separates from alcohol in yellowish crystals and melts at 231°. The *oxime*, $C_8H_7O_2N$, crystallises from hot dilute alcohol and melts at 159°.

1-*o*-Hydroxybenzylidenecoumaranone, $C_{15}H_{10}O_3$, separates from hot dilute alcohol in slender, yellowish crystals melting and decomposing at 208°; it dissolves in alkalis with an intense red colour. 1-*p*-Hydroxybenzylidenecoumaranone is a greenish-yellow, crystalline substance which melts and decomposes at 242°. The two foregoing compounds are substantive dyes.

During the preparation of coumaranone, a considerable quantity of a reddish-brown substance, $C_{16}H_{10}O_3$, is obtained as a bye-product. This has the constitution $C_6H_4 \begin{smallmatrix} \diagup O \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C:C \begin{smallmatrix} \diagup CH_2 \diagdown \\ \diagdown C_6H_4 \diagup \end{smallmatrix} O$, and is probably formed by condensation of 2 mols. of coumaranone.

6-Methylcoumaranone, $C_6H_3Me \begin{smallmatrix} \diagup O \diagdown \\ \diagdown CO \diagup \end{smallmatrix} CH_2$, from *o*-tolylloxyacetic acid, forms yellowish-white crystals melting at 102°, is volatile with steam, and dissolves readily in the common organic solvents or in hot water. With Fehling's solution, it yields a red dye similar to that obtained from coumaranone. The *semicarbazone*, $C_{10}H_{11}O_2N_3$, separates from hot dilute alcohol in yellowish crystals melting at 229°. The *oxime*, $C_9H_9O_2N$, is yellow, dissolves in ether, benzene, or alcohol, and melts at 148°. 1-*o*-Hydroxybenzylidene-6-methylcoumaranone, $C_{16}H_{12}O_3$, crystallises from hot alcohol in yellow needles, dissolves in alkalis, yielding an intense red solution and sublimes and decomposes at 196°. The corresponding *para*-compound forms yellow leaflets which decompose at 210—215°.

5-*Methylcoumaranone*, $C_9H_8O_2$, unlike the analogous substances already described, is an oil, and boils at $106-112^\circ$ under 15 mm. pressure; its properties closely resemble those of coumaranone. The *semicarbazone*, $C_{10}H_{11}O_2N_3$, is yellowish and melts at 208° , the *oxime* $C_9H_9O_2N$, is yellow and melts at 151° . The *o*- and *p*-*hydroxybenzylidene* derivatives, $C_{16}H_{12}O_3$, are yellowish-brown, the former decomposes at 192° , the latter at 212° .

4-*Methylcoumaranone*, $C_9H_8O_2$, is a yellowish liquid which boils without decomposition in a vacuum. The *semicarbazone*, $C_{10}H_{11}O_2N_3$, melts at 181° , and the *oxime*, $C_9H_9O_2N$, at 144° . The *o*- and *p*-*hydroxybenzylidene* derivatives, $C_{16}H_{12}O_3$, decompose at 210° and 163° respectively.

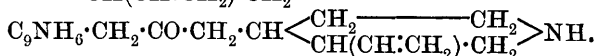
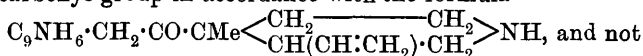
4:6-*Dimethylcoumaranone*, $C_6H_2Me_2 \begin{smallmatrix} \diagup O \diagdown \\ CO \end{smallmatrix} CH_2$, from *as-m*-xylyloxy-acetic acid, melts at 142° . Its *oxime*, $C_{10}H_{11}O_2N$, melts at 148° .

A. L.

The Cinchona Alkaloids. By WILHELM VON MILLER and GEORG ROHDE [in part with JOSEF BRUNNER and ERNST FUSSENEGGER] (*Ber.*, 1900, 33, 3214—3237).—The identity of Pasteur's cinchonine and quinicine (*Jahresber. der Chem.*, 1853, 473) with cinchotoxine and quinotoxine has been established.

By the action of amyl nitrite and sodium ethoxide cinchotoxine is converted into an *isonitroso*-derivative, $C_{19}H_{21}O_2N_3$, which separates in crystal aggregates from chloroform when ether is added, melts at $169-170^\circ$, and, like other secondary piperidine bases, gives a purple coloration with nitrobenzene containing nitrothiophen; the salts do not give this reaction. The *hydrochloride*, $C_{19}H_{21}O_2N_3 \cdot HCl$, melts at 268° , crystallises from alcohol or hot water in prismatic plates, dissolves in acids and alkalis, and gives Liebermann's reaction; the *acetate* melts at 200° , and the *sulphate*, *nitrate*, *formate*, and *phosphate* are also crystalline. The *methiodide*, $C_{19}H_{21}O_2N_3 \cdot MeI$, crystallises from methyl alcohol in prisms and plates, melts at 235° , and, unlike most secondary bases, is not acted on by aqueous alkalis; when treated with sodium ethoxide, it gives a base identical with the *isonitroso*-derivative of methylcinchonine, and it would therefore appear that in the removal of hydrogen iodide from the methiodide the cinchotoxine is reconverted into a cinchonine derivative.

By the action of an excess of amyl nitrite on cinchotoxine, Miller and Rohde's *nitrosoisonitrosocinchotoxine* (*Abstr.*, 1895, i, 433) is produced, and not a *diisonitroso*-derivative; it would therefore appear that cinchotoxine contains only one methylene group adjacent to a carboxyl group in accordance with the formula



The action of *p*-bromophenylhydrazine on quinotoxine gave a mixture of substances, one of which crystallised in yellow aggregates melting at 141° and proved to be a *p*-bromophenylhydrazone, $C_{26}H_{29}ON_4Br$; a second product crystallising in minute yellow

needles and melting 15—20° higher is perhaps the geometrical isomeride.

Nitrosoquinotoxine, $C_{20}H_{23}O_3N_3$, prepared by the action of nitrous acid on quinotoxine, crystallises from a mixture of acetone or benzene with light petroleum in colourless needles, melts at 94°, dissolves in acids and gives Liebermann's reaction; the *phenylhydrazone*, $C_{26}H_{29}O_3N_5$, crystallises from alcohol and melts at 140°. *Nitrosoisonitrosoquinotoxine*, $C_{20}H_{22}O_4N_4$, which is also produced in the action of nitrous acid on quinotoxine, crystallises from alcohol in large, colourless prisms, melts at 186°, and dissolves in alkalis to a yellow solution.

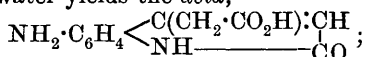
The action of methyl iodide on quinotoxine is similar to its action on cinchotoxine, the products being methylquinine (Claus and Mallmann, *Abstr.*, 1881, 619) and its methiodide; the anhydrous methiodide melts at 180°, not at 215—218°.

iso-Nitrosoquinotoxine, $C_{20}H_{23}O_3N_3$, crystallises from a mixture of alcohol and benzene in yellowish aggregates, melts at 168—170°, and gives the nitrothiopen reaction. The *hydrochloride*, $C_{20}H_{20}O_3N_3 \cdot HCl$, crystallises from alcohol in large tablets and melts at 244°; the *acetate*, *sulphate*, and *nitrate* are crystalline and do not give the nitrothiopen reaction. The *methiodide*, $C_{21}H_{26}O_3N_3I$, crystallises from methyl alcohol, melts at 175°, and is not acted on by aqueous alkalis. By the action of sodium ethoxide the quinine complex is reproduced, the product being an *isonitrosomethylquinine*, which separates as a yellow, amorphous base, melts at 90—100°, and is identical with the base prepared from amyl nitrite and methylquinine; the identity of the bases was also proved by conversion into the *methiodide*, $C_{22}H_{28}O_3N_3I$, melting at 169—170°, and the *nitrate* melting at 175°. T. M. L.

Constitution of Pyridones, Quinolones, and Analogous Bases. By HERMANN DECKER (*J. pr. Chem.*, 1900, [ii], 62, 266—270).—A discussion of the formulæ of pyridones and analogous bases. The author favours formulæ of the ketonic type, $CH \begin{smallmatrix} \diagup CH \cdot CO \\ \diagdown CH : CH \end{smallmatrix} > NR$, which he considers represent the reactions of these bases better than formulæ of the type $\begin{smallmatrix} CH : CH \cdot C \\ | \\ CH : CH \cdot NR \end{smallmatrix} > O$, which contain quinquevalent nitrogen. R. H. P.

Thio-1-methylpyridone and Thio-1-methylquinolone. By ALEXANDER GUTBIER (*Ber.*, 1900, 33, 3358—3359).—*Thio-1-methylpyridone*, $CH \begin{smallmatrix} \diagup CH \cdot CS \\ \diagdown CH : CH \end{smallmatrix} > NMe$, or $S \begin{smallmatrix} \diagup NMe : CH \cdot CH \\ \diagdown C = CH - CH \end{smallmatrix}$, obtained by heating 1-methylpyridone with phosphorus pentasulphide for 4—5 hours at 130°, crystallises from hot water in yellowish-white leaflets, melts at 89—90°, and distils unchanged; it is feebly basic, dissolving in concentrated sulphuric or hydrochloric acid. *Thio-1-methylquinolone*, obtained similarly, forms long, pointed, yellowish green prisms, melts at 118°, boils unchanged above 370°, and resembles the foregoing thiopyridone. Both substances, like 1-methylpyridone and 1-methylquinolone from which they are derived, fail to interact with hydroxylamine in either neutral or alkaline solution. W. A. D.

Action of Ethyl Acetonedicarboxylate on *m*-Phenylenediamine. By EMIL BESTHORN and E. GARBEN (*Ber.*, 1900, 33, 3448—3453. Compare Abstr., 1898, i, 450).—*Ethyl 7-amino-2-quinolone-4-acetate* is obtained when molecular quantities of ethyl acetonedicarboxylate and *m*-phenylenediamine are heated together for several hours in sealed tubes at 100°; on hydrolysis with hydrochloric acid, it yields *7-amino-2-quinolone-4-acetic acid* in the form of its *hydrochloride* which when washed with water yields the *acid*,



this crystallises from water in hair-like, colourless needles melting at about 271°, is only sparingly soluble in the usual organic solvents, and its solution exhibits a blue fluorescence. The *calcium* salt contains 5H₂O, the *ethyl* ester crystallises in needles melting at 197—198°, is sparingly soluble and its solutions also fluoresce. When the acid is rapidly heated at 300°, it loses carbon dioxide and yields *7-amino-lepidone* (*7-amino-2-hydroxylepidine*); when treated with nitrous acid, it yields *7-hydroxy-2-quinolone-4-acetic acid*, which crystallises from hot water in felted needles melting at about 320°; it forms a *hydrochloride* which is decomposed by water, and an *ethyl* ester crystallising in minute needles and melting at 204—205°, but after solidification at above 220°. When the acid is carefully heated, it yields *7-hydroxylepidone* (2 : 7-dihydroxylepidine). J. J. S.

Stereoisomeric Schiff's Bases. By ALEXANDER EIBNER and FRZ. PELTZER (*Ber.*, 1900, 33, 3460—3469. Compare Abstr., 1894, i, 410).—When aqueous solutions of *o*-toluidine and acetaldehyde are mixed and kept at the ordinary temperature for 24 hours, an *ethylidene-o-toluidine*, C₁₈H₂₂N₂, crystallising in small needles and melting, after repeated recrystallisation from alcohol, at 90—92° is obtained; it dissolves readily in both dilute and strong hydrochloric acid, but yields a sparingly soluble *nitrate*; when benzoylated by the Schotten Baumann method, it yields a *benzoyl* derivative, C₂₅H₂₆ON₂, melting at 179°, together with a small amount of the isomeric benzoyl compound melting at 230°. Its *dinitroso*-derivative, C₁₈H₂₀O₂N₄, crystallises in yellow needles melting at 130° and is sparingly soluble in alcohol; when reduced, it yields *p*-phenylenediamine and 2 : 8-dimethyltetrahydroquinoline. When the base is distilled, it yields 2 : 8-dimethylquinoline together with a small amount of the isomeric base melting at 116°.

If the solution of acetaldehyde and *o*-toluidine is warmed, shaken, or kept at the ordinary temperature for several weeks, an *ethylidene-o-toluidine* melting at 116° is obtained; this crystallises in small prisms or plates, is readily soluble in most solvents with the exception of light petroleum, forms a *hydrochloride*, a sparingly soluble *nitrate* melting at 155°, a *diacetyl* derivative melting at 155°, a *dinitroso*-compound melting at 155°, and a *benzoyl* derivative melting at 230°; the latter forms a *nitroso*-compound melting at 190°. The base itself can be distilled without undergoing any great decomposition and is not reduced when treated with sodium and amyl alcohol. The same base is obtained when the isomeride of low melting point is heated for 4 hours at 120—125°, or when its ethereal solution is treated with iodine. When

the condensation takes place in acetic or hydrochloric acid solution, the compound melting at 116° is alone formed. J. J. S.

Action of Nitrosobenzene on Aromatic Hydrazines. By OSKAR SPITZER (*Chem. Centr.*, 1900, ii, 1108; from *Oesterr. Chem. Zeit.*, 3, 489—490).—Whilst by the action of nitrosobenzene on hydrazobenzene, azobenzene and water only are formed, with phenylhydrazine, nitrosobenzene yields, not only these products, but also nitrogen and benzene. The latter reaction may be used to estimate the quantity of nitrogen present as nitroso-groups in organic compounds. E. W. W.

Phenylmethylpyrazolecarboxylic Acids. By CARL BÜLOW (*Ber.*, 1900, 33, 3266—3270).—The acid formerly described by Bülow and Schlesinger as 1-phenyl-3-methylisopyrazole-4:5-dicarboxylic acid (*Abstr.*, 1900, i, 36) is in reality 1-phenyl-5-methylpyrazole-3:4-dicarboxylic acid (compare Stolz, *Abstr.*, 1900, i, 252); it is produced, together with Knorr and Laubmann's dicarboxylic acid (*Abstr.*, 1889, 409), by oxidising 1-phenyl-3:5-dimethylpyrazole-4-carboxylic acid with potassium permanganate; it is identical with the substance produced from diethyl benzeneazodiacetylsuccinate, and yields, by the successive elimination of its carboxyl groups, 1-phenyl-5-methylpyrazole-4-carboxylic acid (m. p. 166°) and 1-phenyl-5-methylpyrazole.

The isomeric acid described by Knorr and Laubmann as melting at 198° has a melting point $203-204^{\circ}$, and is 1-phenyl-3-methylpyrazole-4:5-dicarboxylic acid; it yields 1-phenyl-3-methylpyrazole-4-carboxylic acid (m. p. $192.5-193^{\circ}$) and 1-phenyl-3-methylpyrazole by the successive removal of carboxyl. G. T. M.

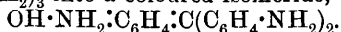
Preparation of Pyrazole Derivatives from Azo-compounds of Diacetosuccinic Esters. By CARL BÜLOW and ALFRED SCHLESINGER (*Ber.*, 1900, 33, 3362—3369).—The following facts form an extension of a previous paper (preceding abstract). Diethyl *p*-tolueneazodiacetosuccinate, $C_6H_4Me \cdot N_2 \cdot CAc(CO_2Et) \cdot C(CO_2Et) : CMe \cdot OH$, obtained by combining *p*-toluenediazonium chloride with ethyl diacetosuccinate, separates from alcohol in yellow crystals, melts at $119-120^{\circ}$, and on boiling with water for 8 hours loses acetic acid (1 mol.), and yields diethyl 1-*p*-tolyl-5-methylpyrazole-3:4-dicarboxylate, $C_6H_4Me \cdot N < \begin{matrix} N= & C \cdot CO_2Et \\ & CMe : C \cdot CO_2Et \end{matrix}$. This crystallises from dilute alcohol, melts at 50° , and on hydrolysis with dilute mineral acids or alkalis yields 1-*p*-tolyl-5-methylpyrazole-3:4-dicarboxylic acid, which forms slender needles, melts at 246° , and yields an acid silver salt, $C_{13}H_{11}O_4N_2Ag$, as a white powder, insensitive to light. On heating the acid above its melting point, it loses carbon dioxide and yields a mixture of 1-*p*-tolyl-5-methylpyrazole and its 4-carboxylic acid. The former is a yellowish oil, which boils at $270-280^{\circ}$, is volatile in steam, and yields a crystalline platinichloride melting and decomposing at 214° ; its 4-carboxylic acid is crystalline, and melts at $199-200^{\circ}$.

Diethyl β -naphthaleneazodiacetosuccinate, prepared from diazotised β -naphthylamine and diethyl acetosuccinate at 0° , separates from dilute alcohol in reddish-yellow crystals and melts at 108° . Diethyl

1-β-naphthyl-5-methylpyrazole-3:4-dicarboxylate crystallises from dilute alcohol in nearly colourless, lustrous leaflets and melts at 82°; the corresponding *dicarboxylic acid* melts at 250°, and on dissolving in ammonia and adding silver nitrate, yields the *silver salt*, $C_{16}H_{11}O_4N_2Ag$, as a heavy, white precipitate. *1-β-Naphthyl-5-methylpyrazole* melts at 65°, boils at 320—330°, and yields a crystalline *platinichloride* melting at 217°. W. A. D.

Theories of Dyeing. By PAUL SISLEY (*Bull. Soc. Chim.*, 1900, [iii], 23, 865—874).—In this paper, the researches of Witt, Knecht, von Georgevics, and Gillet are briefly reviewed, and a description is then given of some fresh experiments favouring Witt's dissolution theory, according to which the dyeing of a fibre is analogous to the extraction of a colouring matter from its aqueous solution by means of an immiscible solvent.

When pure, colourless rosaniline is boiled with water, a coloured solution is obtained which quickly dyes silk; in the presence of excess of alkali (1·5 grams of sodium hydroxide per litre) no coloration is produced. According to Knecht, when silk is dyed with magenta in neutral solution, the exhausted liquid contains the whole of the hydrogen chloride of the dye as ammonium chloride. The author confirms the presence of hydrogen chloride, to some extent, at least, but no ammonia could be detected in the bath. When 100 c.c. of water are boiled with 2 c.c. of normal sodium hydroxide and a little rosaniline, a colourless solution is obtained which dyes silk and yields a red colour to amyl alcohol when boiled therewith. Malachite-green, crystal-violet, and Victoria-blue behave in a similar way; aniline may be used instead of amyl alcohol. These results are shown to be due neither to impurities in the substances employed nor to the action of carbon dioxide. Their explanation is rather to be sought in von Georgevics' hypothesis, according to which the silk, amyl alcohol, or aniline bring about the molecular transformation of the colourless base $OH \cdot C(C_6H_4 \cdot NH_2)_3$ into a coloured isomeride,



The latter does not form a coloured salt with the substance of the fibre, as required by the purely chemical theory of dyeing, but forms either a solid solution with the fibre or a liquid solution with the amyl alcohol or aniline. This view is confirmed by the observations of Hantzsch on colourless and coloured modifications of triphenyl-methane derivatives. Moreover, when silk dyed with rosaniline is boiled with alcohol, the colouring matter is readily dissolved, whilst the fibre does not lose in weight. According to the chemical theory, the alcoholic extract should either be colourless or, if coloured, should contain a portion of the acid substances of the fibre in solution. The fact that in acid solutions animal fibres are dyed with the colour of the alkali salt has been adduced as an argument in favour of the chemical theory of dyeing, the fibre being here held to play the part of a base. It is now shown, however, that amyl alcohol behaves in precisely the same manner as silk in this respect, so that the facts are really in accord with the dissolution theory. Certain facts, however, appear to contradict Witt's view that a colouring matter, in order to be fast,

must necessarily be more soluble in the substance of the fibre than in water. Thus, when silk is dyed with a very dilute solution of a colouring matter, the whole of the latter is extracted from the liquid by the fibre, whereas when a large amount of the dye is used only a comparatively small proportion of it is taken up by the silk. The relative solubilities of the dye in the fibre and in water seem, in fact, to vary greatly with the concentration. Nevertheless, it is believed that experiments now in progress will show that in many cases the behaviour of immiscible solvents is in this respect also identical with that of animal fibres.

N. L.

Coloured Rosaniline Bases. By HUGO WEIL (*Ber.*, 1900, 33, 3141—3144).—In reply to von Georgievics (*Abstr.*, 1900, i, 569), the author adheres to his previous statements (*Abstr.*, 1896, i, 565):

1. That the red precipitate obtained by von Georgievics is really a mixture of rosaniline with a small amount of its hydrochloride.

2. That when a solution of rosaniline carbonate is "salted out" with pure sodium chloride the solution becomes colourless and the clear liquid after concentration gives a blue colour with litmus.

J. J. S.

Relation between the Chemical Constitution of Triphenylmethane Colouring Matters and the Absorption Spectra of their Aqueous Solutions. By PAUL LEMOULT (*Compt. rend.*, 1900, 131, 839—842).—Aqueous solutions of dyes of the triphenylmethane series in all cases give an absorption spectrum which contains a characteristic band of unabsorbed light in the red. The position of the centre of this red space is constant for those dyes which contain two tertiary nitrogen atoms and also for those containing three tertiary nitrogen atoms, but its position in the latter case is quite distinct from that in the former. The solutions employed had a thickness of 6 mm., and contained a gram-mol. of the substance in 1000 litres.

H. R. LE S.

Relation between the Chemical Constitution of the Triphenylmethane Colouring Matters and their Absorption Spectra in Aqueous Solution. By CHARLES CAMICHEL (*Compt. rend.*, 1900, 131, 1001—1002).—The observation made by Lemoult (preceding abstract) relating to the presence of fixed red bands of unabsorbed light in the spectra of triphenylmethane colouring matters containing two or three tertiary nitrogen atoms in the para-position with reference to the methane carbon atom, is only a special case of the law enunciated by Bayrac and the author (*Abstr.*, 1896, ii, 346), who found it to hold for a series of indophenols dissolved in water and other solvents.

The ethereal solution of an indophenol may be advantageously employed as a monochromatic screen instead of red glass.

G. T. M.

The Twelfth Isomeride of Rosinduline. By FRIEDRICH KEHRMANN and G. STEINER (*Ber.*, 1900, 33, 3276—3279. Compare *Abstr.*, 1900, i, 463).—Phenylisonaphthaphenazonium nitrate (*Abstr.*, 1898, i, 154), when left with fuming nitric acid for 24 hours at 0°, yields a

mixture of 2-nitro- and 4-nitro-12-phenylisonaphthaphenazonium nitrates. The former, although sparingly soluble in absolute alcohol, crystallises from dilute alcohol in lustrous, yellow needles, and on reduction yields isorosinduline No. 10 (Abstr., 1900, i, 463), a fact which determines its structure; the latter is easily soluble in alcohol and could not be obtained pure, although the corresponding isorosinduline (No 12) [4-amino-12-phenylisonaphthaphenazonium], formed on reduction, was readily isolated, by taking advantage of the slight solubility of its bromide in saturated aqueous sodium bromide. The salt crystallises in well-formed, nearly black prisms, with a bluish surface-colour; the dichromate is a dark green, microcrystalline powder.

4-Acetylamino-12-phenylisonaphthaphenazonium 12-bromide is very soluble in water, and cannot be separated by saturating the solution with sodium bromide; the chloride, however, crystallises on adding sodium chloride in thick, reddish-brown, prisms or plates, whilst the platinum-chloride forms dark red, granular crystals.

The structure of the isorosinduline No. 12 follows from its synthesis from 5-acetylamino-1:2-naphthaquinone (Kehrmann and Denk, this vol., i, 89). W. A. D.

Constitution of isorosinduline No 9. By FRIEDRICH KEHRMANN and G. STEINER (*Ber.*, 1900, 33, 3280—3284).—Details are given for preparing 2:5-diamino-1:4-naphthaquinoneimide hydrochloride (compare Kehrmann and Haberkant, Abstr., 1899, i, 62) from Ekstrand's naphthapicric acid (2:4:5-trinitro- α -naphthol), the structure of which has recently been determined (Graebe, Abstr., 1900, i, 24; Friedländer, *ibid.*, 150); the salt is much more stable than hitherto thought, not being changed by boiling water. The diamino- α -naphthaquinone and aminohydroxy- α -naphthaquinone derived from it by the action of alkalis have the structures $[O_2 : (NH_2)_2 = 1 : 4 : 2 : 5]$ and $[O_2 : NH_2 : OH = 1 : 4 : 5 : 2]$ instead of those originally given (Abstr., 1899, i, 62). The 5-amino-2-hydroxy-1:4-naphthaquinone is best prepared by heating the hydrochloride in aqueous solution with dilute sulphuric acid; it does not condense with phenyl-o-phenylenediamine in alcoholic or glacial acetic acid solution, but in 80 per cent. acetic acid solution at 100° it yields 4-aminorosindone, $N \equiv C_{10}H_4(NH_2) \rightarrow O$, which was isolated in the form of its acetyl derivative. This crystallises from alcohol in golden needles, melts at 280°, and shows a red fluorescence in alcoholic solution; on warming with dilute sulphuric acid, it yields pure 4-aminorosindone, which crystallises from alcohol in bronze coloured leaflets, melts at 253°, and can also be obtained by the action of cold alcoholic sodium hydroxide on isorosinduline No. 9 (Kehrmann and Filatoff, Abstr., 1900, i, 60). This latter fact, together with the work of Kehrmann and Denk (this vol., i, 89), show that isorosinduline No. 9 is a 4-amino-7-phenyl-naphthaphenazonium. W. A. D.

Constitution of the Naphthapicric Acid melting at 145°. By FRIEDRICH KEHRMANN and G. STEINER (*Ber.*, 1900, 33, 3285—3291).—The trinitro- α -naphthol (naphthapicric acid) melting at 145°

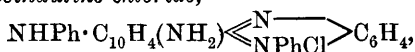
(Kehrmann and Haberkant, Abstr., 1899, i, 62) can be readily separated from its isomeride melting at 190° , on account of the sparing solubility in water of its *sodium* salt, which crystallises in slender, sulphur-yellow needles; the following facts show that it has the constitution $[\text{OH}:(\text{NO}_2)_3=1:2:4:7]$, and the substance formerly described (*loc. cit.*) as 2:6-diamino-1:4-naphthaquinoneimide is therefore a 2:7-diamino-compound. The latter, when warmed with water, yields a mixture of 2:7-diamino-1:4-naphthaquinone with 4:7-diamino-1:2-naphthaquinone, which can readily be removed by extraction with cold 10 per cent. aqueous sodium hydroxide, in the form of the sodium derivative of the tautomeric 7-amino-2-hydroxy-1:4-naphthaquinoneimide. The pure α -quinone forms small prisms which are chocolate-brown with a violet tinge in colour, sublimes and partly decomposes at 230° , yields an orange-yellow *hydrochloride*, and does not combine with ortho-diamines; the β -quinone forms blackish-violet crystals, and yields a violet solution with dilute hydrochloric acid. Both of the quinones when boiled with dilute caustic alkalis yield 7-amino-2-hydroxy-1:4-naphthaquinone along with decomposition products which render purification difficult; the substance isolated forms brownish-red crystals, and combines with *o*-aminodiphenylamine (1 mol.) to form a 2-aminorosindone, $\text{N}=\text{C}_{10}\text{H}_4(\text{NH}_2)\text{C}_6\text{H}_4\text{NPh} \rightarrow \text{O}$, which

yields an *acetyl* derivative crystallising in lustrous, red leaflets melting at $325-335^{\circ}$, identical with the substance formed by the oxidation in the air of an alkaline alcoholic solution of 2-acetylaminophenyl-naphthaphenazonium chloride (Abstr., 1900, i, 463), the latter fact determining its structure.

Confirmatory evidence as to the structure of the new naphthapicric acid is afforded by the fact that the foregoing 4:7-diamino-1:2-naphthaquinone yields with *o*-aminodiphenylamine a 2-aminorosinduline, identical with the substance obtained by acting on 2-acetamino-7-phenyl-naphthaphenazonium chloride (Abstr., 1900, i, 463) with alcoholic ammonia, and subsequently eliminating the acetyl group; the *chloride* forms slender, violet-brown needles, the *acetyl* derivative, $\text{C}_{24}\text{H}_{19}\text{ON}_4\text{Cl}$, crystallises from alcohol in dark-red needles with a brownish sheen, whilst the *dichromate*, $(\text{C}_{24}\text{H}_{19}\text{ON}_4)_2\text{Cr}_2\text{O}_7$, is a red powder.

W. A. D.

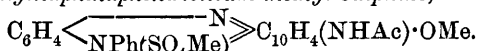
The Thirteenth Isomeride of Rosinduline. By FRIEDRICH KEHRMANN and M. SILBERSTEIN (*Ber.*, 1900, 33, 3300—3307. Compare preceding abstracts).—4-Anilino-6-acetylaminophenyl-1:2-naphthaquinone (Kehrmann and Matis, Abstr., 1899, i, 81) condenses with *o*-aminodiphenylamine hydrochloride in boiling dilute acetic acid solution to form principally 3-acetylaminophenylrosinduline chloride (3-acetylaminophenyl-5-anilino-7-phenyl-naphthaphenazonium chloride), along with a small quantity of the isomeric 12-phenylisonaphthaphenazonium chloride; the latter separates first in brownish-red needles, and will be described in a later communication, whilst the former is obtained only on salting out. It crystallises from alcohol in thick, dark-red prisms with a golden sheen, and with dilute alcoholic sodium hydroxide yields the *base*, $\text{C}_{30}\text{H}_{23}\text{ON}_4\cdot\text{OH}$, in brownish-red leaflets with a bronze-like lustre.

3-Aminophenylrosinduline chloride,

separates on boiling the acetyl derivative with alcoholic hydrochloric acid, in thick crystals with a greenish lustre; from solutions containing an excess of hydrochloric acid, the *hydrochloride*, $\text{C}_{28}\text{H}_{22}\text{N}_4\text{Cl}_2$, is obtained.

3-Aminorosindone, $\text{N} \begin{array}{c} \text{C}_{10}\text{H}_4(\text{NH}_2) \\ \text{C}_6\text{H}_4 \cdot \text{NPh} \end{array} \text{O}$, is formed on heating

3-acetyl-amino-7-phenylrosinduline chloride with 10 per cent. sulphuric acid for 2—3 hours at $175\text{--}180^\circ$; the *acetyl* derivative crystallises from acetic anhydride in vermilion-red needles with a greenish, metallic lustre, does not melt or decompose at 310° , and unites with methyl sulphate in nitrobenzene solution at 150° to form 3-acetyl-amino-5-methoxy-7-phenylnaphthaphenazonium methyl sulphate,



This is precipitated on adding ether as an orange, crystalline powder, which regenerates rosindone on boiling with water containing a trace of alkali, and yields a *platinichloride*, $(\text{C}_{25}\text{H}_{20}\text{O}_2\text{N}_3)_2\text{PtCl}_6$, as an orange-yellow, flocculent precipitate; on warming with alcoholic ammonia, evaporating, extracting with water, and adding sodium bromide, 3-acetylaminorosinduline bromide separates. It crystallises from boiling alcohol in vermilion needles with a greenish lustre, and yields an insoluble microcrystalline *dichromate*, $(\text{C}_{24}\text{H}_{19}\text{ON}_4)_2\text{Cr}_2\text{O}_7$; on elimination of the amino-group by the diazo-reaction, it forms 3-acetyl-amino-7-phenylnaphthaphenazonium, isolated as the *chloride* in the form of an orange powder, sparingly soluble in water, which in dilute aqueous solution yields, on adding nitric acid, microscopic red needles of the *nitrate*. *isoRosinduline* No. 13 (3-amino-7-phenylnaphthaphenazonium) was obtained by heating the foregoing chloride with 50 per cent. sulphuric acid; the *bromide* forms olive-green needles and dissolves in water with a brownish-red, but in alcohol with a dark-green, coloration. It is somewhat unstable in solution, yielding aminorosindone on boiling; alcoholic ammonia converts it into aminorosinduline.

The above indirect method of obtaining *isorosinduline* No. 13 became necessary because 6-acetyl-amino-1:2-naphthaquinone with *o*-amino-diphenylamine yields only the isomeric *isorosinduline* No. 7 (Abstr. 1899, i, 525).

W. A. D.

Osmophoric Groups.* By HANS RUPE and KARL VON MAJEWSKI (Ber., 1900, 33, 3401—3408).—The principal “osmophoric” groups are —OH , =O , —CHO , —COMe , —OMe , —NO_2 , —CN , —N_3 (triazole). Analogous compounds containing —CHO , —NO_2 , —CN , —N_3 have similar odours.

Piperonylamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{:O}_2\text{:CH}_2$, obtained by treating piperonylonitrile with hydrogen peroxide, crystallises in lustrous prisms or needles, melts at 169° , in common with piperonylonitrile has a similar odour to piperonal, and, when treated with bromine and

* A name chosen by the authors to designate those groups the presence of which predicates an odorous substance.

sodium hydroxide, yields *p*-aminocatechol methylene ether, which is a white, crystalline substance, melts at 44—46°, boils at 144° under 16 mm. pressure, and forms a hydrochloride, and an acetyl derivative melting at 135°. Triazopyrocatechol methylene ether, $N_3 \cdot C_6H_4 \cdot O_2 \cdot CH_2$, obtained from the hydrochloride just mentioned, crystallises in yellow leaflets, melts at 128—130° and has a faint odour like piperonal as well as the anise-like odour of all triazo- (azoimide) compounds.

Methyl *p*-triazobenzoate, $N_3 \cdot C_6H_4 \cdot CO_2Me$, obtained by the method described in the next abstract, crystallises in large, yellow laminæ, is volatile with steam, melts at 39—40°, and has a characteristic sweet anise-like odour, very similar to that of methyl *p*-cyanobenzoate; the latter ester forms colourless leaflets melting at 62°. Methyl *m*-triazobenzoate and methyl *o*-triazobenzoate are light yellow oils having odours similar to (but weaker than) that of the *p*-compound. *p*-Triazoanisole crystallises in yellowish-white laminæ melting at 36°, and *o*-triazoisole is a heavy, yellow oil, both having odours similar to those of the triazobenzoates. *p*-Triazobenzaldehyde is a colourless liquid with a strong, pleasant, anise-like odour; *p*-triazobenzonitrile, however, has hardly any odour and crystallises in colourless needles, which melt at 70°. *p*-Triazoacetanilide forms colourless crystals and melts at 124°.

m-Hydroxyacetophenone, obtained by the diazotisation of *m*-aminoacetophenone and decomposition of the resulting diazo-compound, crystallises in colourless laminæ, melts at 95°, forms a methyl ether, which is a colourless oil boiling at 128—129° under 12 mm. pressure, and unlike the analogous *o*- and *p*-compounds has hardly any odour. *m*-Cyanoacetophenone crystallises in small, white needles, melts at 98—99°, and has no odour; the corresponding *m*-acetylbenzoic acid crystallises in slender, white needles, melts at 172°, is odourless, and forms a methyl ester, which is a colourless, odourless oil; *m*-triazooacetophenone is a yellow, odourless oil.

R. H. P.

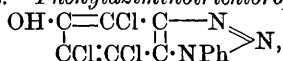
Preparation of Azoimides (Triazo-compounds). By HANS RUPE and KARL VON MAJEWSKI (*Ber.*, 1900, 33, 3408—3410).—The azoimides corresponding with weak bases are most conveniently prepared by treating a solution of a diazo-salt with potassium hydroxylaminedisulphonate. The method gave good results with *p*-nitroaniline, *m*-nitroaniline, methyl *p*-aminobenzoate, and *p*-bromoaniline. *p*-Triazobromobenzene forms crystals melting at 20° and has a pleasant aromatic odour. Hydroxylamine hydrochloride may be used instead of potassium hydroxylaminedisulphonate, but the results are not quite so good.

R. H. P.

Ketochlorides and Quinones of Phenylaziminobenzene [Phenylbenzotriazole]. By THEODOR ZINCKE and E. PETERMANN (*Annalen*, 1900, 313, 251—298. Compare Abstr., 1899, i, 135).—

Phenylaziminopentachloroketotetrahydrobenzene, $\begin{array}{c} CO-CCl_2-C-N \\ | \quad | \quad | \\ CCl_2 \cdot CHCl \cdot C \cdot NPh \end{array} \gg N$, prepared by the action of chlorine on phenylaziminoaminobenzene (Nietzki, Abstr., 1896, i, 164), crystallises in lustrous, colourless needles, and melts at 128—129°; it liberates iodine from potassium iodide, and develops an intense red coloration with aniline.

Phenylaziminotetrachloroketodihydrobenzene, $\begin{array}{c} \text{CO}-\text{CCl}_2\text{C}-\text{N} \\ \text{CCl}_2\text{C}-\text{C}-\text{NPh} \end{array} \gg \text{N}$, obtained when the foregoing substance is heated alone or with potassium acetate, dissolves readily in organic media, and decomposes when attempts are made to recrystallise it; the compound melts at 173—174°, liberates iodine from potassium iodide, and develops an intense red coloration with aniline. *Phenylaziminotrichlorophenol*,



formed on reducing the last-named substance with stannous chloride, crystallises from glacial acetic acid in pale yellow needles, which melt and decompose at 227°; the *acetyl* derivative forms colourless needles and melts at 128°. *Phenylaziminodichlorophenol*, $\begin{array}{c} \text{OH}\cdot\text{C}=\text{CCl}\cdot\text{C}-\text{N} \\ \text{CCl}\cdot\text{CH}\cdot\text{C}-\text{NPh} \end{array} \gg \text{N}$, obtained by reducing the pentachloroketone with stannous chloride, crystallises in colourless, prismatic needles, and melts at 177—178°.

Phenylaziminodichloro-o-quinone, $\begin{array}{c} \text{CO}-\text{CO}-\text{C}-\text{N} \\ \text{CCl}\cdot\text{CCl}\cdot\text{C}-\text{NPh} \end{array} \gg \text{N}$, is formed from trichlorophenol and tetrachloroketone on oxidation with nitric acid, and crystallises in reddish-yellow leaflets having a golden lustre; it melts and decomposes at 210°, and gives a bluish-green solution in sodium hydroxide. The *anilino*-derivative, $\text{C}_{18}\text{H}_{11}\text{O}_2\text{N}_4\text{Cl}$, $\text{C}_6\text{H}_7\text{N}$, purified by precipitation with water from solutions in alcohol or acetic acid, melts and decomposes at 130—140°; the *azine*, $\text{C}_{18}\text{H}_9\text{N}_5\text{Cl}_2$, prepared from the quinone and *o*-phenylenediamine, crystallises in silky needles, and melts above 250°.

Phenylaziminodichlorocatechol, $\begin{array}{c} \text{OH}\cdot\text{C}:\text{C}(\text{OH})\cdot\text{C}-\text{N} \\ \text{CCl}\cdot\text{CCl}\cdot\text{C}-\text{NPh} \end{array} \gg \text{N}$, formed when the quinone is reduced with stannous chloride, crystallises from glacial acetic acid in slender, pale red needles which melt and decompose at 217°; the *diacetyl* derivative forms colourless needles and melts at 187°.

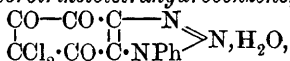
Phenylaziminochlorocatechol, $\begin{array}{c} \text{OH}\cdot\text{C}:\text{C}(\text{OH})\cdot\text{C}-\text{N} \\ \text{CCl}\cdot\text{CH}\cdot\text{C}-\text{NPh} \end{array} \gg \text{N}$, the other product of reducing the quinone, melts and decomposes at 214—215°.

Phenylaziminochlorohydroxy-p-quinone, $\begin{array}{c} \text{OH}\cdot\text{C}-\text{CO}-\text{C}-\text{N} \\ \text{CCl}\cdot\text{CO}\cdot\text{C}-\text{NPh} \end{array} \gg \text{N}$, prepared by the action of sodium carbonate on the dichloro-*o*-quinone, crystallises in lustrous, yellow needles which melt and decompose at 223°; the *acetyl* derivative forms lustrous, yellow needles melting at 135—136°, whilst the *anilino*-derivative, $\text{C}_{18}\text{H}_9\text{O}_3\text{N}_4\text{Cl}$, and the *eurhodol*, $\text{C}_{18}\text{H}_{10}\text{ON}_5\text{Cl}$, decompose at 180° and 200° respectively.

Phenylaziminotetraketotetrahydrobenzene, $\begin{array}{c} \text{CO}\cdot\text{CO}-\text{C}-\text{N} \\ \text{CO}\cdot\text{CO}\cdot\text{C}-\text{NPh} \end{array} \gg \text{N}$, obtained on oxidising the *p*-quinone with nitric acid, crystallises from the concentrated acid in colourless needles which become yellow in light, and melt and decompose at 175°; the *diazine*, $\text{C}_{24}\text{H}_{13}\text{N}_7$, is sparingly soluble in common media, and melts above 260°.

Phenylaziminodihydroxy-p-quinone,
$$\begin{array}{c} \text{OH} \cdot \text{C} \cdot \text{CO} \cdot \text{C} - \text{N} \\ \text{OH} \cdot \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{NPh} \end{array} \gg \text{N},$$
 formed when the tetraketone is dissolved in sodium carbonate, is a red powder which gradually darkens above 200° , and melts, decomposing, at about 254° .

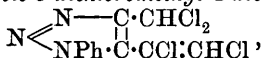
Phenylaziminodichlorotriketotetrahydrobenzene,



produced when chlorine is passed into a solution of the chlorohydroxy-*p*-quinone in acetic acid, crystallises in small, white needles and melts, decomposing, at 150 — 151° ; the *azine*, $\text{C}_{18}\text{H}_{19}\text{ON}_5\text{Cl}_2$, crystallises from glacial acetic acid in grey, lustrous needles, which sinter above 210° , and decompose at 238° .

The *acid*, $\text{N} \ll \begin{array}{c} \text{N} - \text{C} \cdot \text{CHCl}_2 \\ \text{NPh} \cdot \text{C} \cdot \text{CCl} \cdot \text{CO}_2\text{H} \end{array}$ or $\text{N} \ll \begin{array}{c} \text{N} - \text{C} \cdot \text{CCl}_2 \cdot \text{CO}_2\text{H} \\ \text{NPh} \cdot \text{C} \cdot \text{CCl} \cdot \text{CHCl} \end{array}$, prepared from the pentachloroketone by the action of dilute sodium hydroxide, and of bleaching powder in either acid or alkaline solution, crystallises from alcohol in colourless needles melting at 148° ; the *sodium* salt forms transparent prisms, and the *methyl* ester melts at 124° .

1-Phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic (*n*-phenylpyrro-1 : 2-diazole-dicarboxylic, phenylaziminoethylenedicarboxylic) *acid*, $\text{N} \ll \begin{array}{c} \text{N} - \text{C} \cdot \text{CO}_2\text{H} \\ \text{NPh} \cdot \text{C} \cdot \text{CO}_2\text{H} \end{array}$, resulting from the oxidation of the foregoing acid with potassium permanganate, has been already described by Michael (Abstr., 1893, i, 570). *1-Phenyl-4-dichloromethyl-5-dichloroethylene-1 : 2 : 3-triazole* (*n*-phenylimino-1 : 2-diazole-3-dichloromethyl-4-dichloroethylene),



produced when the monocarboxylic acid is heated alone or with acetic anhydride, crystallises from glacial acetic acid and melts at 95 — 96° .

The *ad-diketocarboxylic acid*, $\text{N} \ll \begin{array}{c} \text{N} - \text{C} \cdot \text{CO} \cdot \text{CO}_2\text{H} \\ \text{NPh} \cdot \text{C} \cdot \text{CO} \cdot \text{CHCl}_2 \end{array}$, prepared by the action of sodium carbonate on the dichlorotriketone, crystallises in lustrous, colourless needles which darken above 105° , and melt and decompose at 130° ; phenylhydrazine converts it into the *diphenylhydrazone*, $\text{C}_{24}\text{H}_{18}\text{O}_5\text{N}_7\text{Cl}$, which forms reddish-brown, crystalline granules sintering above 110° .
M. O. F.

4-Methyldeoxyxanthine and Deoxyheteroxanthine. By JULIUS TAFEL and ARTHUR WEINSCHENK (*Ber.*, 1900, 33, 3369—3377. Compare Abstr., 1900, i, 121; ii, 588).—When 4-methylxanthine is dissolved in 50 per cent. sulphuric acid and reduced electrolytically at 1 — 14° between prepared lead electrodes with a current concentration of 120 amperes, the *sulphate* of 5-oxy-4-methyl-6 : 7-dihydropurine (4-methyldeoxyxanthine) separates; this salt and the *picrate* were analysed. The base itself crystallises with $1\text{H}_2\text{O}$, and decomposes at 210 — 220° without melting; although neutral in reaction to litmus, it dissolves in dilute alkalis. It is oxidised by bromine in acetic acid solution

(lead peroxide is not suitable) to 5-oxy-4-methylpurine; this base and its sulphate and picrate were prepared, and the last two were analysed.

Heteroxanthine was also reduced in the manner just described; in this case no sulphate separates. The product, 5-oxy-1-methyl-6:7-dihydropurine (deoxyheteroxanthine), decomposes at 260—264° without melting; it is feebly alkaline to litmus, and does not dissolve in dilute alkalis; the hydrochloride, sulphate, and picrate were prepared and analysed. The base is oxidised either by lead peroxide or by bromine, in acetic acid solution, to 5-oxy-1-methylpurine (E. Fischer, Abstr., 1899, i, 175).
C. F. B.

Isomeric Change of Azoxybenzene. By EUGEN BAMBERGER (*Ber.*, 1900, 33, 3192—3193).—When azoxybenzene is converted into *p*-hydroxyazobenzene by warm sulphuric acid (Wallach and Belli, Abstr., 1880, 556), a very small quantity of *o*-hydroxyazobenzene is formed and may be isolated by the process already described (see following abstract).
A. L.

Action of Diazobenzene on Phenol and Synthesis of *o*-Hydroxyazobenzene. By EUGEN BAMBERGER (*Ber.*, 1900, 33, 3188—3192).—*o*-Hydroxyazobenzene is obtained in small quantity by the action of diazobenzene on phenol and may be separated from the para-derivative by distillation with steam and purified by means of its copper salt, which is very sparingly soluble in alcohol. It is identical with the substance obtained from nitrosobenzene (Abstr., 1900, i, 531).

o-Methoxyazobenzene, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{Ph}$, is obtained on adding *o*-anisidine to nitrosobenzene dissolved in acetic acid. It crystallises in groups of orange-red, compact needles melting at 40—41°, dissolves readily in most organic media even in the cold, and is converted into *o*-hydroxyazobenzene by aluminium chloride.

o-Hydroxybenzeneazo-*p*-toluene, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Me}$, produced in small quantity when *p*-diazotoluene reacts with phenol, crystallises from boiling water in thin, shining, irregular yellow tablets or leaflets with a bronzed lustre melting at 100—105°. It dissolves readily in organic solvents and sparingly in water. Its solution in alkali is orange-red. The copper salt, which is sparingly soluble in boiling alcohol, forms brown, silky needles which have a green, metallic lustre. On reduction with zinc dust and aqueous ammonium chloride, the dye is converted into *o*-aminophenol and *p*-toluidine.
A. L.

Composition of Proteids. By ALBRECHT KOSSEL and W. KUTSCHER (*Zeit. physiol. Chem.*, 1900, 31, 165—214).—An important contribution to proteid chemistry, but which hardly admits of abstraction. Important quantitative results concerning the way in which different fractions of the nitrogen are combined, and the yield of such decomposition products as amino-acids, ammonia, hexon bases, &c., are given, together with quantitative methods. Protamines, proteids proper, and albuminoids are all brought under review.
W. D. H.

Decomposition Products of Proteids. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1900, 31, 214—226).—Hausmann's method (Abstr.,

1899, i, 653; 1900, i, 317) of determining the way in which the nitrogen is combined in proteids is untrustworthy. W. D. H.

NOTE BY ABTRACTOR.—This has been pointed out previously by Y. Henderson (Abstr., 1900, i, 265).

The Carbohydrate Group of Crystallised Egg-Albumin. By LEO LANGSTEIN (*Zeit. physiol. Chem.*, 1900, 31, 49—57).—It is shown that the reducing substance which can be obtained from crystallised egg-albumin is glucosamine. The direct action of concentrated mineral acid on egg-albumin does not split off the reducing substance, because of the simultaneous production of ammonia. After treatment with alkali, as Pavy first showed, the reducing substance is obtainable. W. D. H.

The Phosphorus of Nucleins. By ALBERTO ASCOLI (*Zeit. physiol. Chem.*, 1900, 31, 156—160).—Neither in leuco-nuclein nor in casein is any of the phosphorus contained in the form of metaphosphoric acid. W. D. H.

A New Decomposition Product of Yeast Nuclein. By ALBERTO ASCOLI (*Zeit. physiol. Chem.*, 1900, 31, 161—164).—Thymin has been obtained from the nucleic acid from thymus, spleen, salmon sperm, and herring roe. The amount of material hitherto obtained from yeast nuclein did not admit of analysis. In the present research, thymin was obtained by W. Jones' method (Abstr., 1900, i, 572) from thymus, and a similar material from yeast nuclein; the latter substance was not thymin, but uracil. W. D. H.

Constitution of Thymin. By H. STEUDEL (*Zeit. physiol. Chem.*, 1900, 30, 539—541. Compare Abstr., 1900, i, 467). When thymin is methylated by Hoffmann's method (Abstr., 1890, 31) a product, $C_5H_4Me_2O_2N_2$, is obtained which is isomeric with Behrend's trimethyl-uracil (Abstr., 1886, 339). It crystallises from alcohol in needles melting at 153° .

When thymin is nitrated and then reduced, a substance is obtained which gives Weidel's reaction with chlorine water and ammonia; the author concludes that the presence of a pyrimidine ring in thymin is thus established. J. J. S.

Antipeptone. By FR. KUTSCHER (*Ber.*, 1900, 33, 3457—3460).—A polemical paper in reply to Siegfried (this vol., i, 57). J. J. S.

Expressed Yeast-cell-plasma (Buchner's Zymase). By EDUARD BUCHNER (*Ber.*, 1900, 33, 3311—3315).—The author criticises several of the numerical results obtained by Macfadyen, Morris, and Rowland (this vol., i, 59), and points out that the considerable amount of autofermentation observed by them was probably due to the presence of glycogen in the juice. The juice obtained by the author underwent very little autofermentation, the amount of carbon dioxide thus evolved being always less than one-tenth of that evolved in the presence of sugar. A. H.

Organic Chemistry.

Composition of Shale Naphtha. By BASIL STEUART (*J. Soc. Chem. Ind.*, 1900, 19, 986—989).—The olefines were removed by successive treatment with concentrated sulphuric acid and aqueous sodium hydroxide, and the aromatic hydrocarbons by shaking with a mixture of sulphuric and nitric acids; the nature and amount of the olefines were not determined, but they appear to be present in larger quantity than in natural petroleum. After the foregoing treatment, the naphtha boiling between 20° and 105° was repeatedly fractionated. *n*-Hexane was by far the principal hydrocarbon present, traces only of *isohexane* being found, along with, possibly, methylpentamethylene; the *n*-hexane was purified by heating for three days with fuming nitric acid, when the latter was found to contain propionic and succinic acids with a trace of oxalic acid. *n*-Heptane and *isohexane* were present to a considerable extent but could not be separated from one another by fractional distillation; the high values for the sp. gr. of the heptane fractions between 89° and 100° appear to indicate the presence of, possibly, both hexamethylene and methylhexamethylene and the absence of dimethylpentamethylene. The difficulty experienced in separating the *n*-heptane and *isohexane* may be due to the presence of the isomeric γ -ethylpentane (triethylmethane) boiling at 96°, but this hydrocarbon has not yet been identified in American or Russian petroleum.

n-Pentane was present in small proportion compared with the hexanes and heptanes, and *isopentane* in small proportion to *n*-pentane. The sp. gr. and vapour density of a small fraction boiling between 48° and 57° appear to indicate the presence in small quantities of pentamethylene; a small fraction boiling between 38° and 42° similarly appeared to contain methyltetramethylene.

The greatest proportion of benzene was found in the original fractions boiling between 70° and 75° and 65° and 70°, and was separated as *m*-dinitrobenzene; the fraction 75—80° contained only traces of benzene, owing to the bulk of the latter having distilled at a lower temperature along with the hexane (compare Young and Jackson, *Trans.*, 1898, 73, 922). Benzene appears to constitute 2.6 per cent. of the original fractions boiling between 55° and 75°; it is probable, however, that an additional quantity may have been removed by the preliminary treatment to eliminate olefines. Toluene forms about the same proportion of the fraction from 95—105°, its distilling below its boiling point being due to the presence of heptane (compare *loc. cit.*).

W. A. D.

Electrolytic Synthesis of Organic Substances. By KARL ELBS and FRITZ FOERSTER (*Zeit. Elektrochem.*, 1900, 7, 341).—A reply to Dony-Hénault (*Abstr.*, 1900, i, 577) with reference to the electrolytic formation of iodoform.

T. E.

Derivatives of Tetradecylacetylene. By FRIEDRICH KRAFFT and G. HEIZMANN (*Ber.*, 1900, 33, 3586—3590. Compare Abstr., 1892, 1163).—*Tetradecylacetylene tetrabromide*, $C_{14}H_{29} \cdot CBr_2 \cdot CHBr_2$, a colourless liquid which cannot be distilled under 15 mm. pressure, is prepared by mixing together tetradecylacetylene and bromine at a low temperature and then gradually heating the mixture to 60° . The *copper* compound, $C_{14}H_{29} \cdot C \equiv C \cdot Cu \cdot OH$, is a greenish-grey substance produced by shaking together the hydrocarbon and ammoniacal cuprous chloride solution; the *mercurichloride*, $C_{14}H_{29} \cdot C \equiv C \cdot HgCl$, is a white compound, whilst the *mercuro-nitrate*, $C_{14}H_{29} \cdot C \equiv C \cdot Hg_2 \cdot NO_3$, is white, turning grey on exposure to light. The *sodium* derivative, $C_{14}H_{29} \cdot C \equiv CNa$, is a yellowish-white substance regenerating the hydrocarbon on treatment with water or methyl alcohol.

Nitrotetradecylacetylene, $C_{16}H_{29} \cdot NO_2$, produced by slowly adding fuming nitric acid to tetradecylacetylene cooled to -16° , yields *amino-tetradecylacetylene*, $C_{14}H_{29} \cdot C \equiv C \cdot NH_2$, on reduction with zinc dust and acetic acid; this base is a white, crystalline mass melting at $41-42^\circ$, and boiling at 195° under 15 mm. pressure; its *platinichloride* forms a yellow, flocculent precipitate.

Tetradecylacetylenesulphonic acid, $C_{14}H_{29} \cdot C \equiv C \cdot SO_3H$, is obtained in the form of its barium salt, $(C_{16}H_{29}SO_3)_2Ba$, by mixing the hydrocarbon with concentrated sulphuric acid, neutralising the solution with dilute sodium hydroxide solution, precipitating the sulphonate by means of sodium chloride, redissolving this product in hot water, and reprecipitating with barium chloride.

Tetradecylacetylenecarboxylic acid (*tetradecylpropionic acid*), $C_{14}H_{29} \cdot C \equiv C \cdot CO_2H$, prepared by passing carbon dioxide over sodium tetradecylacetylde heated at 120° , crystallises from dilute methyl alcohol in white leaflets melting at $44-45^\circ$; when distilled under 15 mm. pressure, it decomposes into carbon dioxide and tetradecylacetylene. Silver nitrate in aqueous ammoniacal solution forms the *silver* salt, $C_{14}H_{29} \cdot C \equiv C \cdot CO_2Ag$.

Tetradecylpropionamide, $C_{14}H_{29} \cdot C \equiv C \cdot CO \cdot NH_2$, produced by adding a mixture containing equivalent proportions of phosphorus pentachloride and the acid to cold concentrated ammonia, crystallises from absolute alcohol in leaflets melting at $76-77^\circ$; the *benzoyl* derivative melts at $114-115^\circ$.

Tetradecylbenzoylacetylene, $C_{14}H_{29}C \equiv C \cdot C \cdot OPh$, a very unstable ketone, it obtained by condensing crude tetradecylpropionic chloride with benzene in the presence of aluminium chloride; it distils at 145° in a high vacuum, and solidifies to a yellowish-white, waxy mass. G. T. M.

Presence of Methyl Alcohol in the Fermented Juice of several Fruits. By JULES WOLFF (*Compt. rend.*, 1900, 131, 1323—1324. Compare Abstr., 1899, ii, 387).—The fermented juice of black currants, plums, mirabelles, cherries, apples, or grapes contains methyl alcohol, but the unfermented juice does not, except black currant juice, which contains it in small quantities. Rum and whisky do not contain methyl alcohol, but traces of it are present in brandy.

H. R. LE S.

Absence of Methyl Alcohol in Rum. By HENRI QUANTIN (*J. Pharm.*, 1900, [vi], 12, 505—507. Compare Abstr., 1899, ii, 387, and preceding abstract).—Formaldehyde, methyl formate, and methyl alcohol were found to be absent from the distillates obtained by the fractional distillation of 85 hectolitres of rum. H. R. LE S.

Hydrolysis of Ethyl Nitrate by Water. By EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 656—667).—The solubility of ethyl nitrate in 100 parts of water between 55° and 85° is given by the following formula, in which t represents the temperature: $2.2239 - 0.03642 t + 0.0003512 t^2$.

The hydrolysis of ethyl nitrate was studied in an aqueous solution kept saturated at 70°. The reaction is unimolecular, so that if x be the quantity of nitric acid formed after a time, θ (hours), and K the velocity constant of the reaction, $dx/d\theta = K$, whence $K = (x - x_0)/\theta$. The results show that the value of K increases from about 0.134 when $\theta = 5$ to 0.150 when $\theta = 114$, indicating that the nitric acid formed exerts an accelerating influence on the hydrolysis. Taking k_1 as the constant of the hydrolysis of ethyl nitrate by water and k_2 as that of the accelerating action of the nitric acid, C representing the constant concentration, the velocity of the reaction is represented by: $dx/d\theta = (k_1 + k_2)C$. The values of k_1 and k_2 calculated on the basis of the above measurements are: $k_1 = 0.004246$, which means that in a solution of constant concentration water hydrolyses in 1 hour 0.004246 of the total quantity of ethyl nitrate present; $k_2 = 0.0135$ (for normal acid), the total action of the acid and water being given by the constant $(k_1 + k_2) = 0.0177$. Other experiments with non-saturated solutions of ethyl nitrate, with and without the addition of nitric acid, confirm these numbers. These results are quite different from those obtained in the hydrolysis of esters of organic acids; thus Ostwald (Abstr., 1884, 581), in determining the velocity of hydrolysis of methyl acetate by normal nitric, hydrochloric, and other acids, did not take into account the action of the water present. From numbers given by Ostwald, it is seen that at 25° water hydrolyses in 30 days some 20—25 per cent. of the methyl acetate in solution, whilst with the same initial concentration of the ester, normal acetic acid hydrolyses 67 per cent. in the same time. The ratio between these two velocities is of the same order as in the hydrolysis of ethyl nitrate by nitric acid, although the actual velocities are widely different in the two cases. T. H. P.

Action of Ethyl Iodide on Silver Nitrate. By EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1900, 30, 667—673).—When ethyl iodide is gradually added to powdered silver nitrate, the mixture being kept cool, nearly the theoretical yield of ethyl nitrate is obtained. In presence of water, however, part of the ethyl nitrate formed is converted into alcohol and nitric acid (see preceding abstract), whilst if the reaction is carried out in absolute alcoholic solution, ether and nitric acid are formed along with the ethyl nitrate, as has been already shown by Nef (Abstr., 1900, i, 4). The results of Bertrand (*Bull. Soc. Chim.*, 1880, 33, 556), who, on boiling ethyl iodide in absolute alcohol with silver nitrate, obtained ethyl nitrate and nitrite and acetaldehyde, are explained by the fact that he distilled off the excess of alcohol

and ethyl nitrate from the resultant products, the nitric acid thus being concentrated and acting on the remaining alcohol according to the equation: $2\text{EtOH} + \text{HNO}_3 = \text{MeCHO} + \text{EtNO}_2 + 2\text{H}_2\text{O}$. Nef (*loc. cit.*) explains the action of silver nitrate on ethyl iodide in alcoholic solution as due to the preliminary formation of methylene derivatives, caused by the splitting off of hydrogen and iodine atoms from the same carbon atom of the ethyl iodide, this and the subsequent reactions being expressed by the following equations: (1) $\text{Me}\cdot\text{CH}_2\text{I} \rightleftharpoons \text{Me}\cdot\text{CH} + \text{HI}$, (2) $\text{HI} + \text{AgNO}_3 = \text{AgI} + \text{HNO}_3$, (3) $\text{Me}\cdot\text{CH} + \text{HNO}_3 = \text{Me}\cdot\text{CH}_2\cdot\text{NO}_3$, (4) $\text{Me}\cdot\text{CH} + \text{Me}\cdot\text{CH}_2\cdot\text{OH} = \text{Et}_2\text{O}$. According to this view, the whole reaction should be unimolecular, since reaction (2), being ionic, has an immense velocity, and removes all the hydrogen iodide formed by reaction (1), which would hence proceed to an end. It has, however, been shown by Chiminello (*Abstr.*, 1896, ii, 354) that the action of ethyl iodide on silver nitrate is bimolecular at 0° , although at higher temperatures, where the reaction proceeded much more rapidly, the velocity constant calculated for a bimolecular reaction was found to increase appreciably; this increase is shown by the author to be due to the rapid development of heat by the reaction, and the consequent heating of the solutions, since by using solutions with less concentration, in which the velocity of reaction is correspondingly diminished, he finds the reaction to be strictly bimolecular. From these considerations and also from the facts (1), that in the reaction in which *tert*-butyl iodide takes part (also considered by Nef) no dissociation with formation of a methylene derivative is possible, and (2), that with propyl iodide and silver nitrate in alcoholic solution, ethyl propyl ether is obtained, whilst with *isopropyl* iodide, ethyl *isopropyl* ether is formed, whereas Nef's scheme would lead to the formation of ethyl *isopropyl* ether in both cases, the author concludes that Nef's views are erroneous and that the action of ethyl iodide on silver nitrate is one of double decomposition. The formation of ether in this reaction is assumed to be due to the action of alcohol on the ethyl nitrate *in statu nascendi*.

T. H. P.

α -Chlorovaleric Acids. By LÉON SERVAIS (*Bull. Acad. Roy. Belg.*, 1900, 695—724).— α -Hydroxyvaleronitrile, formed by the interaction of butaldehyde with hydrogen cyanide, readily reacts with phosphorus pentachloride to form α -chlorovaleronitrile, $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CN}$, a slightly yellow liquid boiling at 161° . α -Chlorovaleric acid, obtained on hydrolysis with concentrated hydrochloric acid, melts at -15° , boils at 132 — 135° under 32 mm. and at 222° under 763 mm. pressure, has a sp. gr. 1.141 at 13.2° , n_D 1.44807 at 11° , and is insoluble in water. The chloride, $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{COCl}$, is a pungent, fuming liquid; it boils at 155 — 157° under 763 mm. pressure, and has a sp. gr. 1.246. Ethyl α -chlorovalerate is a colourless oil with an agreeable mint-like odour; it boils at 185° under 752 mm. pressure, has a sp. gr. 1.040 at 11.8° , and n_D 1.43071 at 11° .

α -Chloroisovaleronitrile, $\text{CHMe}_2\cdot\text{CHCl}\cdot\text{CN}$, obtained from α -hydroxyisovaleronitrile and phosphorus pentachloride, boils at 154 — 155° under 750 mm. pressure; the corresponding bromo-derivative distils and decomposes at 175 — 180° under a pressure of 754 mm. α -Chloro-

isovaleric acid is a crystalline mass which melts at 16° and boils at $125\text{--}126^{\circ}$ under 32 mm., and at $210\text{--}212^{\circ}$ with slight decomposition under 756 mm. pressure; it has a sp. gr. 1.135 at 13.2° and n_D 1.44496 at 11° . The *chloride*, $\text{CHMe}_2\cdot\text{CHCl}\cdot\text{COCl}$, is a pungent liquid of sp. gr. 1.135 at 13.2° , and boils at $148\text{--}149^{\circ}$ under 759 mm. pressure. *Ethyl α -chloroisovalerate* has a penetrating, mint-like odour, boils at $177\text{--}179^{\circ}$ under 756 mm. pressure, has a sp. gr. 1.021 at 13.2° and n_D 1.42951 at 11° .

α -Chloro- α -methylbutyronitrile, $\text{CMeEtCl}\cdot\text{CN}$, prepared by the action of phosphorus pentachloride on the cyanohydrin derived from methyl ethyl ketone, is a colourless, mobile liquid which boils unchanged at $55\text{--}60^{\circ}$ under 32 mm. and at $120\text{--}135^{\circ}$ with decomposition under 762 mm. pressure; it has a sp. gr. 0.8969 at 15° . *α -Chloro- α -methylbutyric acid* boils at $123\text{--}124^{\circ}$ under 36 mm. pressure, has a sp. gr. 1.101 at 10° and n_D 1.45077 at 11° ; it distils at $200\text{--}205^{\circ}$ under 754 mm. pressure, with loss of hydrogen chloride, and crystals of a methylcrotonic acid (?) separate from the distillate. The *chloride*, $\text{CMeEtCl}\cdot\text{COCl}$, is a fuming liquid, boiling at $143\text{--}144^{\circ}$ under 749 mm. pressure, and having a sp. gr. 1.187 at 14° . *Ethyl α -chloro- α -methylbutyrate* boils at 175° under 747 mm. pressure, has a sp. gr. 1.069 at 14° , and n_D 1.43683 at 11° .

The relationship between the boiling points of these compounds is discussed at some length. W. A. D.

Preparation of the Higher Acid Anhydrides ($\text{C}_n\text{H}_{2n-1}\text{O}$)₂O. By FRIEDRICH KRAFFT and W. ROSINY (*Ber.*, 1900, 33, 3576—3579). —The anhydrides of the higher fatty acids are readily obtained by the action of the acid chlorides on the alkali salts when these compounds are thoroughly dried and purified.

n-Heptoic anhydride, $(\text{C}_7\text{H}_{13}\text{O})_2\text{O}$, is a colourless, oily liquid boiling at 164.5° under 15 mm. pressure; it solidifies on cooling, and melts at 17° ; it has a characteristic odour resembling that of ozone, and absorbs moisture from the atmosphere, becoming converted into *n*-heptoic acid.

n-Octoic anhydride, $(\text{C}_8\text{H}_{15}\text{O})_2\text{O}$, boils at 186° under 15 mm. pressure, and melts at -1° .

n-Nonoic anhydride, $(\text{C}_9\text{H}_{17}\text{O})_2\text{O}$, forms a white, crystalline mass melting at 16° and boiling at 207° under 15 mm. pressure.

n-Lauric anhydride (*n-dodecoic anhydride*), $(\text{C}_{12}\text{H}_{23}\text{O})_2\text{O}$, obtained in hard, white crystals melting at 41° , boils at 166° when distilled by the aid of von Babo's mercury-air pump.

Myristic anhydride (*tetradecoic anhydride*), $(\text{C}_{14}\text{H}_{27}\text{O})_2\text{O}$, forms white crystals, melts at 51° , and boils at 198° in a high vacuum.

Palmitic anhydride (*hexadecoic anhydride*) is a white solid, the melting point of which lies close to that of palmitic acid.

Phenylheptadecenoic acid, $\text{C}_6\text{H}_5\cdot\text{C}_{16}\text{H}_{30}\cdot\text{CO}_2\text{H}$, prepared by heating a mixture of benzaldehyde, palmitic anhydride, and dry sodium palmitate up to 170° , crystallises in slender needles and melts at $87\text{--}88^{\circ}$; the replacement of palmitic anhydride by acetic anhydride lessens the yield and purity of the product. The *silver* salt, $\text{C}_{23}\text{H}_{25}\text{O}_2\text{Ag}$, obtained by adding silver nitrate to the ammoniacal solution of the acid,

forms a voluminous precipitate which becomes crystalline on repeated washing. G. T. M.

Action of Reducing Agents on the Two Isomeric Ethyl Nitrodimethylacrylates. By LOUIS BOUVEAULT and A. WAHL (*Compt. rend.*, 1900, 131, 1211—1213. Compare this vol., i, 4).—The α isomeride, $\text{CMe}_2\cdot\text{C}(\text{NO}_2)\cdot\text{CO}_2\text{Et}$, yields ethyl dimethylacrylate when treated with stannous chloride or tin and hydrochloric acid, and gives rise to products very soluble in water by the action of sodium sulphite or bisulphite. Sodium nitrodimethylacrylate is produced from the ester by the action of sodium and moist ether, and the acid set free by the action of hydrochloric acid loses carbon dioxide and gives rise to a nitroisobutylene, probably identical with the product of direct nitration (Haitinger, *Abstr.*, 1879, 700).

Ethyl aminodimethylacrylate, $\text{CMe}_2\cdot\text{C}(\text{NH}_2)\cdot\text{CO}_2\text{Et}$, produced by the action of aluminium amalgam on a moist ethereal solution of the α -nitro-ester, is a colourless liquid with an unpleasant odour; it boils at 93—95°, and has a sp. gr. 1.018 at 0°/4°. The compound is basic, and dissolves in dilute acids; it is slightly soluble in water and is miscible with the ordinary organic solvents. Its *carbamide* and *phenylcarbamide* crystallise in needles melting respectively at 175—176° and 130°.

isoPropenylphenylhydantoin, $\text{CO}\left\langle\begin{smallmatrix}\text{NH}\cdot\text{CMe}_2 \\ \text{—NHPH—}\end{smallmatrix}\right\rangle\text{CO}$, obtained by boiling the phenylcarbamide with dilute alcohol, melts at 225—226°.

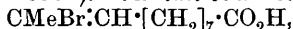
Phenylcarbamino dimethylacrylic acid, produced by the action of sodium hydroxide solution on the phenylcarbamide, melts at 195—196°; the reaction also gives rise to a certain amount of the preceding compound. G. T. M.

Condensation of Ketones with Ethyl Cyanoacetate. By GUSTAV KOMPPA (*Ber.*, 1900, 33, 3530—3534).—An ice-cold mixture of pure, dry acetone (1 mol.), and ethyl cyanoacetate (2 mols.), when treated with a few drops of diethylamine, undergoes condensation which is complete after the mixture has been left at the ordinary temperature for a month, and then gradually heated on the water-bath for several hours; when distilled under 10 mm. pressure, it yields a fraction boiling at 100—120°, consisting mainly of ethyl dimethylmethylenecyanoacetate, and a fraction 120—175° containing mainly ethyl dimethylmethylenedicyanoacetate.

Ethyl dimethylmethylenecyanoacetate [*ethyl α -cyano- β -methylcrotonate*], $\text{CMe}_2\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, is a colourless, mobile oil distilling at 108° under 10 mm. pressure, and solidifying to a crystalline mass melting at 28°, and readily soluble in all organic solvents. It is readily oxidised, but does not combine with bromine.

Ethyl dimethylmethylenedicyanoacetate, [*ethyl $\alpha\alpha'$ -dicyano- $\beta\beta$ -dimethylglutarate*], $\text{CMe}_2[\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}]_2$, is a thick oil distilling at 186—188° under 10 mm. pressure; it crystallises from ether and light petroleum in four-sided plates melting at 53—54°. With sodium ethoxide, it yields a yellow, crystalline *sodium* derivative; when hydrolysed with 50 per cent. sulphuric acid, it yields $\beta\beta$ -dimethyl glutaric acid. J. J. S.

Transformation of κ -Undecenoic Acid into θ -Undecenoic Acid and Brassylic Acid. By FRIEDRICH KRAFFT and R. SELDIS (*Ber.*, 1900, 33, 3571—3575).— *ι -Bromo- θ -undecenoic acid*,



prepared by saturating a carbon disulphide solution of undecolic acid (m. p. $59\cdot5^\circ$) at 50° with hydrogen bromide, is an oil solidifying at low temperatures and boiling with slight decomposition at 202° under 16 mm. pressure. *θ -Undecenoic acid*, $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$, obtained by reducing the preceding compound in alcoholic solution with sodium containing a trace of mercury, aluminium, or iron, boils at 165° under 10 mm. pressure, and melts below 19° . The new acid is distinguished from its isomeride, κ -undecenoic acid, by its lower melting point and by its behaviour towards an acetic acid solution of chromium trioxide, the former compound yielding azelaic acid, whilst the latter gives rise to sebacic acid. The θ -acid forms a *dibromide*, $\text{C}_{11}\text{H}_{20}\text{Br}_2\text{O}_2$, an *amide*, $\text{C}_{11}\text{H}_{19}\text{ONH}_2$, melting at 86 — 87° , an insoluble *silver salt*, and a *barium salt* closely resembling that of the κ -isomeride.

Komppa (*Abstr.*, 1900, i, 201) successively prepared from methyl bromo-undecate by the malonic ester synthesis a methyl diethyl undecanetricarboxylate boiling at 223 — 224° under 10 mm. pressure, an oily undecanetricarboxylic acid, and a normal undecamethylenedicarboxylic acid melting at 82° ; as this dicarboxylic acid appeared to be isomeric and not identical with brassylic acid, he concluded that the latter must contain a branched chain. The authors find, on repeating this work, that the tricarboxylic ester boils at 233 — 234° under 10 mm. pressure, and that the acid is a solid which, on heating, yields brassylic acid melting at 113 — 114° , and corresponding in every respect with the product obtained from erucic acid. G. T. M.

Derivatives of the Higher Unsaturated Carboxy-acids. By FRIEDRICH KRAFFT and F. TRITSCHLER (*Ber.*, 1900, 33, 3580—3585).— *κ -Undecenoic chloride*, $\text{C}_{10}\text{H}_{19}\cdot\text{COCl}$, obtained in quantitative yield by the action of phosphorus pentachloride on κ -undecenoic acid, is an oil boiling at $128\cdot5^\circ$ under 14 mm. pressure; the *anhydride*, $(\text{C}_{11}\text{H}_{19}\text{O})_2\text{O}$, produced by heating together a mixture of the preceding compound and dry sodium undecenoate, melts at 13 — $13\cdot5^\circ$, and boils at 170 — 179° in a high vacuum; its *tetrabromide*, $(\text{C}_{10}\text{H}_{19}\text{Br}_2\cdot\text{CO})_2\text{O}$, melts at $36\cdot5^\circ$. *κ -Undecenamide*, $\text{C}_{11}\text{H}_{19}\text{O}\cdot\text{NH}_2$, prepared by treating the chloride with ice-cold aqueous ammonia, crystallises in white scales and melts at 87° . *κ -Undecenonitrile*, $\text{C}_{10}\text{H}_9\cdot\text{CN}$, produced when the amide is warmed with phosphorus pentachloride, boils at 129 — 130° under 14 mm. and at 257° under the ordinary pressure.

Amino- κ -undecylene, $\text{C}_{11}\text{H}_{21}\cdot\text{NH}_2$, a colourless liquid solidifying in a freezing mixture and boiling at 123° under 16 mm. pressure and at 238 — 240° under the ordinary pressure, is formed by reducing κ -undecenonitrile with sodium and absolute alcohol; its *benzoyl* derivative crystallises from benzene in leaflets, and melts at 41 — 42° ; its *phenylthiocarbamide* forms colourless leaflets melting at 48° .

Diundecenylthiocarbamide, produced from the base and carbon disulphide, crystallises in white leaflets and melts at $50\cdot5^\circ$. *Undecenamidoxime*, $\text{C}_{10}\text{H}_{19}\cdot\text{C}(\text{NH}_2)\cdot\text{NOH}$, formed by the addition of hydroxyl-

amine to the nitrile, crystallises from benzene in lustrous, white leaflets melting at 69° .

Elaidic chloride, $C_{17}H_{33}\cdot COCl$, is a colourless, slightly fuming liquid boiling with partial decomposition at 216° under 13 mm. pressure; it solidifies in a freezing mixture; its *amide* melts at $89-90^{\circ}$; *elaidonitrile* melts at -1° , and boils at $213-214^{\circ}$ under 16 mm. pressure.

Elaidamine, $C_{18}H_{35}\cdot NH_2$, forms a white, crystalline mass melting at 25° and boiling at $194-195^{\circ}$ under 13 mm. and at $338-340^{\circ}$ under the ordinary pressure; it rapidly absorbs carbon dioxide from the air. The *hydrochloride* crystallises in lustrous, white scales, and decomposes at 185° ; the *platinichloride* and the *benzoyl* derivative form yellow scales and lustrous leaflets respectively, the latter melting at $63-64^{\circ}$. *Dielaitylthiocarbamide*, $CS(NH\cdot C_{18}H_{35})_2$, and *phenylelaitylthiocarbamide*, $C_{18}H_{35}NH\cdot CS\cdot NHPh$, crystallise in white leaflets melting respectively at 73° and 65° .

Oleic chloride is a colourless liquid boiling at 213° under 13.5 mm. pressure; the *amide* melts at 75° , and yields elaidonitrile on treatment with phosphorus pentachloride.

Brassic chloride, $C_{21}H_{41}\cdot COCl$, yields the *amide* melting at 94° . *Brass-onitrile*, $C_{21}H_{41}\cdot CN$, melts at $21-22^{\circ}$ to a colourless, inodorous liquid boiling at 257° under 17 mm. pressure. *Brassamine*, $C_{22}H_{43}\cdot NH_2$, melts at $45-46^{\circ}$, and boils at 250° under 11 mm. pressure; its *benzoyl* derivative crystallises in lustrous leaflets and melts at $74-75^{\circ}$; the *hydrochloride* and *platinichloride* are described, the former melting and decomposing at 130° . *Erucamide*, melting at $78-79^{\circ}$, when treated with phosphorus pentachloride, yields brass-onitrile.
G. T. M.

Lactic Acid in Beet-molasses. By A. SCHÖNE and BERNHARD TOLLENS (*Zeit. Ver. deut. Zuckerind.*, 1900, 980—981).—Lactic acid is invariably found in beet-molasses, and owes its origin to the boiling of the sucrose solution with lime in the process of defecation. T. H. P.

Action of Amyl Formate on Ethyl Sodiocynoacetate. By E. GRÉGOIRE DE BOLLEMONT (*Bull. Soc. Chim.*, 1901, [iii], 25, 15—18).—The principal product of the action of amyl formate on ethyl sodiocynoacetate at 100° is not ethyl formylcynoacetate, which might be expected to be formed, but a *compound*, $CN\cdot C(\cdot CH\cdot ONa)\cdot CO_2\cdot C_5H_{11}$, in the production of which an interchange of the amyl and ethyl groups has taken place, whilst the formyl group must be considered, from analogy with homologous compounds (see following abstracts), to have assumed the enolic form. The *barium* salt, $(C_9H_{12}O_3N)_2Ba$, in which form the compound was isolated, crystallises in nacreous leaflets, and the *silver* salt in tufts of slender needles. The former is identical with the barium salt obtained from the product of the action of amyl formate on amyl sodiocynoacetate.
N. L.

Ethoxy- and Methoxy-methylenecyanoacetic Esters. By E. GRÉGOIRE DE BOLLEMONT (*Bull. Soc. Chim.*, 1901, [iii], 25, 18—28).—The following compounds were prepared by heating together molecular proportions of ethyl (or methyl) orthoformate with various alkyl cyanoacetates in the presence of acetic anhydride.

Ethyl ethoxymethylenecyanoacetate [α -cyano- β -ethoxyacrylate]

$\text{OEt}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, from ethyl cyanoacetate and ethyl orthoformate, crystallises from boiling alcohol in large, colourless needles melting at $52-53^\circ$ and boiling at $190-191^\circ$ under 30 mm. pressure. The *methyl* ester crystallises from alcohol in large, transparent tablets melting at 28° and boiling at about 200° under 32 mm. pressure; it has a sp. gr. 1.1255 at $23^\circ/4^\circ$. Determinations of the molecular refraction and dispersion of this compound, both in the pure state and when dissolved in toluene, gave values considerably higher than those calculated from Brühl's data, a result which is probably to be explained by the presence of the ethylenic linking. The *propyl* ester forms large, colourless crystals melting at 31° and boiling at 189° under 15 mm. pressure. The *amyl* ester could only be obtained as an oily liquid boiling at about 211° under 35 mm. pressure.

Methyl methoxymethylenecyanoacetate [α -cyano- β -methoxyacrylate], $\text{OMe}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Me}$, obtained by the action of methyl orthoformate on methyl cyanoacetate and also by the action of methyl iodide on the silver derivative, $\text{OAg}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Me}$, derived from methyl cyanoethoxyacrylate, crystallises in slender needles melting at 88° and boiling at 185° under 25 mm. pressure. The *ethyl* ester crystallises in small prisms melting at 99° and boiling at 190° under 17 mm. pressure.

All these esters are only slightly soluble in water, but more or less soluble in organic solvents. Their aqueous solutions, when treated with barium hydroxide, yield the corresponding barium salts, whilst with ammonia or aniline, amides or anilides are obtained. N. L.

Hydroxymethylenecyanoacetic Esters. By E. GRÉGOIRE DE BOLLEMONT (*Bull. Soc. Chim.*, 1901, [iii], 25, 28—38).—These compounds are readily obtained by treating the corresponding ethoxy- and methoxy-cyanoacrylates (see preceding abstract) with barium hydroxide and decomposing the barium salts thus obtained with sulphuric acid. The alkyl hydroxycyanoacrylates are strong acids, capable of displacing acetic acid from its salts, and readily estimated alkalimetrically. They are slightly soluble in water, but more soluble in alcohol or ether. The lower members of the series crystallise well; all undergo more or less decomposition when distilled under diminished pressure. Their aqueous solutions give an intense orange-brown coloration with ferric chloride.

Methyl hydroxymethylenecyanoacetate [α -cyano- β hydroxyacrylate], $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Me}$, has a pungent odour and melts at $136-137^\circ$. Determinations of the electric conductivity of the sodium salt at 25° gave a result $\mu_{1024-32} = 12.01$, approaching the value (11.3) usually found for the salts of monobasic acids. The affinity coefficient (K 1.505) of the ester itself shows that it must be considered as a strong organic acid, occupying a position between chloroacetic and dichloroacetic acids. The *barium*, *copper*, and *silver* salts have been prepared and analysed; they are well crystallised compounds. The *ethyl* ester crystallises in colourless plates melting at 69° and has a less pronounced acid character than the preceding compound. The *barium* and *copper* salts have been prepared and analysed. The *amyl* ester could only be obtained

in an impure state. The barium and silver salts of this ester have already been described (preceding abstracts). N. L.

Transformation of *O*-Acyl Derivatives of Ethyl Acetoacetate into the Isomeric *C*-Acyl Derivatives. By LUDWIG CLAISEN and E. HAASE (*Ber.*, 1900, 33, 3778—3784).—Acetophenone acetal, $\text{CH}_3\cdot\text{CPh}(\text{OEt})_2$, can be converted into *iso*acetophenone ethyl ether, $\text{CH}_3\cdot\text{CPh}\cdot\text{OEt}$, and this is transformed into phenyl propyl ketone, $\text{CH}_2\text{Et}\cdot\text{CPhO}$, when it is boiled under a pressure of two atmospheres (*Abstr.*, 1897, i, 188). It has not been found possible in any way to effect a similar transformation with ethyl β -ethoxycrotonate (ethyl *O*-ethylacetoacetate), $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CMe}\cdot\text{OEt}$. On the other hand, ethyl *O*-acetylacetoacetate, $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CMe}\cdot\text{OAc}$, is converted into ethyl diacetoacetate, $\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CMeO}$ or $\text{CO}_2\text{Et}\cdot\text{CHAc}_2$, when it is dissolved in ethyl acetate (a little ethyl acetoacetate being added) and heated with potassium carbonate on the water-bath. A similar transformation can be effected with *methyl O*-acetylacetoacetate, which was prepared in like manner to the ethyl ester (*Abstr.* 1900, i, 373), boils at 95° under 17 mm. pressure, and has sp. gr. 1.1006 at 18° ; the *copper* derivative of methyl diacetoacetate melts at $226\text{--}227^\circ$, and does not decompose from 200° onwards, as stated previously (*Abstr.*, 1894, i, 32).†

Without the addition of a little ethyl acetoacetate, the reaction takes place very slowly. The authors assume that even then a little of this substance is first formed, and then brings about the reaction described, first forming the potassio-derivative by means of the potassium carbonate present. "The transformation of the *O*-acetate by potassium carbonate into the potassium salt of the *C*-acetyl derivative is effected by means of a small quantity of ethyl potassioacetoacetate. The *O*-acetate reacts with this, forming ethyl potassiodiacetoacetate and ethylacetoacetate; and the regenerated ethyl acetoacetate reacts again as before." This view is borne out by the fact that ethyl sodioacetate and *O*-acetylacetate give a good yield of diacetoacetate when heated together on the water-bath. The transformation in question is analogous to that of sodium phenyl carbonate into sodium salicylate; such a migration of an acyl group from an O to a C atom is rare, however. Probably the formation of *C*-acyl derivatives of ethyl acetoacetate when the sodium derivative of this substance is treated with acid chlorides is to be explained, as a rule, in the same way, an *O*-acyl derivative being formed at first, and then undergoing transformation. C. F. B.

Decomposition of Normal Ammonium Oxalate. By HENRI GILLOT (*Bull. Acad. Roy. Belg.*, 1900, 744—767).—On boiling an aqueous solution of ammonium oxalate, the whole of the ammonia is progressively evolved, somewhat rapidly at first and more slowly later; in the case of a solution of 0.151 gram of the salt in 750 c.c. of water, elimination is complete after boiling for 15 hours, the source of heat being an oil-bath at $130\text{--}140^\circ$. The oxalic acid simultaneously undergoes partial decomposition into carbon dioxide and formic acid. At 70° , the decomposition of ammonium oxalate by water takes place

very slowly, whilst at 50° it ceases altogether. Cold, dry air does not alter the composition of the hydrated salt, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$; dry air at 65° , however, gradually expels the water of crystallisation, but not the ammonia; exposure of either the hydrated or anhydrous salt to moist air for $3\frac{1}{2}$ months at $19-22^{\circ}$ yields a salt containing approximately $2.7\text{H}_2\text{O}$ without ammonia being lost. This stability towards air is noteworthy, since most other ammonium salts, under similar conditions, lose a large part of their ammonia.

Aqueous solutions of ammonium oxalate evolve ammonia when exposed to light, the action being proportional to the intensity of illumination; thus, in bright sunlight after 46 days, 2.30 per cent. of the salt was decomposed; in diffused light, 0.85 per cent.; and in darkness, only 0.42 per cent. W. A. D.

Cineolic Acid. Resolution of *n*-Cineolic Acid into its Optically Active Components. By HANS RUPE and MAX RONUS (*Ber.*, 1901, 33, 3541—3546. Compare Abstr., 1900, i, 371).—Strychnine *d*-cineolate, $\text{C}_{31}\text{H}_{36}\text{O}_6\text{N}_2$, crystallises from hot water in large, compact prisms which melt at $195-197^{\circ}$. The mother liquors from this salt, on further evaporation, yield successively the salts of the inactive and lævo-acids.

d- and *l*-Cineolic acids separate from water in large, transparent crystals which melt at 79° and contain $1\text{H}_2\text{O}$. The anhydrous acids, obtained by exposure of the hydrated crystals in dry air, melt at $138-139^{\circ}$, and have $[\alpha]_D +18.56$ and -19.10 respectively at 20° in aqueous solution. They are readily soluble in water, alcohol, or cold chloroform (unlike the racemic acid, which is sparingly soluble in chloroform); when crystallised from dry ethyl acetate or ether, they separate in the form of aggregated leaflets. The difference in solubility of the racemic and active acids in water is remarkable; the former dissolves in 133.3 parts of water at 8° , the latter in 11.2. The crystals of the *l*-acid belong to the rhombic system, $[a:b:c = 0.9815:1:1.4771]$.

It has been observed on more than one occasion that the active acids undergo auto-racemisation when crystallised, but no explanation of this is forthcoming. It was frequently observed, too, that on recrystallising the *d*-acid from water, an acid in the form of large plates or prisms, containing $1\text{H}_2\text{O}$ and melting at $123-126^{\circ}$, was formed, but after dehydration had the same melting point as the original acid.

d-Cineolic anhydride, $\text{C}_{10}\text{H}_{14}\text{O}_4$, boils at $165-167^{\circ}$ under 15 mm. pressure, dissolves sparingly in light petroleum, and crystallises from cold benzene in large, transparent, six-sided tablets melting at 108° . In benzene solution, it gave $[\alpha]_D +45.37$ at 20° . A. L.

Attempted Synthesis of $\alpha\beta$ -Trimethylglutaric Acid. By G. BLANC (*Bull. Soc. Chim.*, 1901, [iii], 25, 68—73).—When $\beta\beta$ -dimethylævulic acid is treated with hydrocyanic acid, and the cyanohydrin thus produced is hydrolysed, the lactonic acid, $\beta\beta\gamma$ -trimethylpentane- $\alpha\gamma$ -olidic acid, $\text{CMe}_2\text{CH}_2\text{CH}(\text{CO}_2\text{H})\text{CO}$, is obtained, which crystallises from water in small, colourless prisms melting at $163-164^{\circ}$. This acid has the same melting point as the isomeric lactonic acid,

$\text{CMe}_2 \begin{cases} \text{CH}(\text{CO}_2\text{H}) \cdot \text{O} \\ \text{CHMe} \text{---} \text{CO} \end{cases}$, which Balbiano (Abstr., 1900, i, 202) obtained by the oxidation of camphoric acid with potassium permanganate, but the two acids are essentially different, since a mixture of them melts between 110° and 120° . Moreover, the calcium and barium salts of the acid now described crystallise with 4 and $5\text{H}_2\text{O}$ respectively, whereas the corresponding salts of Balbiano's acid crystallise with 2 and $4\text{H}_2\text{O}$. Attempts to obtain $\alpha\beta\beta$ -trimethylglutaric acid by reducing the new lactonic acid with hydriodic acid were unsuccessful, however the experimental conditions were varied, although Balbiano's acid is stated to be readily reduced. This difference in the behaviour of the two acids is probably due to the fact that in the one the lactonic oxygen is connected with a tertiary carbon, and in the other to a secondary carbon atom. N. L.

New Formal (Methylene) Compounds of Hydroxy-acids. By WILLIAM ALBERDA VAN EKENSTEIN (*Proc. K. Acad. Amst.*, 1900, 3, 400—403. Compare Weber and Tollens, Abstr., 1898, i, 61).—Formaldehyde reacts with certain hydroxy-acids in aqueous solution, and methylene derivatives are produced which differ from those already known, inasmuch as the carboxyl group takes part in the condensation. These compounds are obtained by the repeated evaporation of the solutions of the hydroxy-acids with excess of formaldehyde; the yield is small, and the product is separated from the unaltered material by extraction with ether, chloroform, or benzene.

The compound, $\begin{matrix} \text{O} \cdot \text{CO} & & \text{CO} \cdot \text{O} \\ | & & | \\ \text{CH}_2 \cdot \text{O} & \text{---} & \text{O} \cdot \text{CH}_2 \end{matrix} \text{CH} \cdot \text{CH}$, obtained from *d*-tartaric acid, crystallises in white needles, melts at 117° , and has $[\alpha]_D 112^\circ$; the substance has a neutral reaction and is hydrolysed by acids or alkalis. Mesotartaric acid yields a similar compound which melts at 106° and is inactive; racemic acid, however, does not interact with formaldehyde.

The compound, $\begin{matrix} \text{CH}_2 \cdot \text{O} \\ | \\ \text{O} \cdot \text{CO} \end{matrix} \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$, from citric acid, melting at 200° , may be titrated in the cold as a dibasic acid. The oily compound obtained from malic acid contains one methylene group and is laevorotatory.

Formaldehyde has no action on salicylic and oxalic acids in aqueous solution, but it certainly reacts with the sugars, for their optical rotation is greatly affected, that of dextrose being doubled; the rotatory powers of galactose, lævulose, arabinose, and mannose are considerably decreased, whilst *d*-rhamnose becomes laevorotatory. The methylene compounds of these carbohydrates are very unstable and have not been isolated.

Benzaldehyde seems to interact with the sugars and hydroxy-acids in a similar manner, but the products are oily and unstable.

G. T. M.

Dilactones. By RUDOLPH FITTIG (*Annalen*, 1900, 314, 1—96. Compare Abstr., 1898, i, 11).—[With ERNST ROTH]—The ketodi-

lactone of β -acetylglutaric acid, $\text{CO} \begin{array}{c} \text{O} \text{---} \text{CMe} \text{---} \text{O} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{CO}$, prepared by heating dried sodium tricarballoylate with acetic anhydride ($1\frac{1}{2}$ mols.) at $120\text{--}130^\circ$ during 36 hours, melts at 99° , and is identical with the substance described by Emery (Abstr., 1897, i, 325); it is completely hydrolysed when boiled with water during 24 hours. According to Emery's statement, β -acetylglutaric acid melts at $47\text{--}50^\circ$, but the author has obtained it in aggregates of long leaflets melting at 58° ; it is best prepared by converting the dilactone into the calcium salt, decomposing the aqueous solution with two-thirds the calculated quantity of hydrochloric acid, and allowing the ethereal extract to evaporate spontaneously. The *calcium* salt contains $3\text{H}_2\text{O}$, and the *silver* salt is anhydrous. The aniline derivative of the ketodilactone crystallises in leaflets and needles, and melts at 149° ; according to Emery, the substance melts at $153\text{--}154^\circ$.

Valerolactoneacetic acid, $\text{CO} \begin{array}{c} \text{O} \text{---} \text{CHMe} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$, prepared by reducing the ketodilactone with sodium amalgam, crystallises from chloroform in aggregates of small needles and melts at 84° ; according to Emery, the substance melts at $78\text{--}79^\circ$. The *barium* salt is amorphous, and the *calcium* salt contains $2\text{H}_2\text{O}$. *Hydroxyethylglutaric acid*, $\text{OH} \cdot \text{CHMe} \cdot \text{CH}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$, arising from valerolactoneacetic acid on hydrolysis, has not been isolated, the lactone being regenerated very easily; the *barium*, *calcium*, and *silver* salts are anhydrous.

[With WILHELM STERNBERG].—The *ketodilactone* of benzylidene- β -acetylglutaric acid, $\text{CO} \begin{array}{c} \text{O} \text{---} \text{CMe} \text{---} \text{O} \\ \text{C}(\text{:CHPh}) \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{CO}$, obtained by heating dried sodium tricarballoylate with acetic anhydride ($1\frac{1}{2}$ mols.) and benzaldehyde (1 mol.), crystallises in lustrous leaflets, and melts at 162° ; the *dibromide*, $\text{C}_{14}\text{H}_{12}\text{O}_4\text{Br}_2$, crystallises from hot benzene in small needles, and melts and decomposes at 163° . *Benzylidene- β -acetylglutaric acid*, $\text{C}_{14}\text{H}_{14}\text{O}_5$, obtained by hydrolysing the dilactone, is converted into that substance so readily that it has not been isolated; the *calcium* salt contains $1\frac{1}{2}\text{H}_2\text{O}$, the *barium* salt $1\text{H}_2\text{O}$, and the *silver* salt is anhydrous.

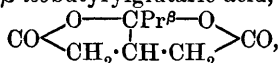
When the ketodilactone of benzylidene- β -acetylglutaric acid is reduced with sodium amalgam, two isomeric substances, $\text{C}_{14}\text{H}_{14}\text{O}_4$, are produced. The *α -ketodilactone* crystallises from benzene and melts at 134° ; hydrolysis converts it into a benzyl- β -glutaric acid, of which the *calcium* and *barium* salts contain $2\text{H}_2\text{O}$, whilst the *silver* salt is anhydrous. The *β -ketodilactone* crystallises from alcohol in stellate aggregates of leaflets, and melts at 169° ; the *calcium* salt of the benzyl- β -glutaric acid, which it yields on hydrolysis, contains $2\frac{1}{2}\text{H}_2\text{O}$, the *barium* salt $4\text{H}_2\text{O}$, and the *silver* salt is anhydrous.

[With ERNST ROTH].—The ketodilactone of benzylidene- β -acetylglutaric acid is also produced when dried sodium β -acetylglutarate is heated with benzaldehyde and acetic anhydride.

[With TOM GUTHRIE].—The *ketodilactone* of β -butyrylglutaric acid, $\text{CO} \begin{array}{c} \text{O} \text{---} \text{CPr}^a \text{---} \text{O} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{CO}$, produced on heating dried sodium tricar-

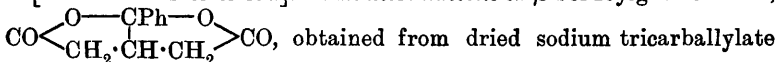
allylate with butyric anhydride at 125° during 12 hours, crystallises in needles on adding ether or petroleum to the solution in chloroform, and melts at 55° . β -Butyrylglutaric acid, $\text{COPr}^{\alpha}\cdot\text{CH}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, crystallises in prisms or leaflets, and is readily soluble in water or alcohol; it melts at 88° , and belongs to the monoclinic system [$\beta = 58^{\circ}30'$]. The barium salt contains $2\text{H}_2\text{O}$, the calcium salt $2\frac{1}{2}\text{H}_2\text{O}$, and the silver salt is anhydrous. Heptolactoneacetic acid, $\text{CO} \begin{array}{c} \text{O} - \text{CHPr}^{\alpha} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array} \text{CO}$, formed when the ketodilactone is reduced with sodium amalgam, crystallises in rosettes of white needles and melts at 53° ; the crystals belong to the monoclinic system [$a:b = 1.5443:1$; $\beta = 78^{\circ}56'$]. The calcium salt contains $2\text{H}_2\text{O}$, the barium and silver salts being anhydrous. Heptolactoneacetic acid is hydrolysed with difficulty, but the protracted action of concentrated barium hydroxide solution yields the dibasic acid, $\text{C}_9\text{H}_{16}\text{O}_5$, which could not be isolated; the calcium, barium, and silver salts are anhydrous.

The ketodilactone of β -isobutyrylglutaric acid,

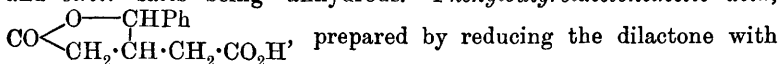


prepared from dried sodium tricarballoylate and isobutyric anhydride, melts at $89-90^{\circ}$. β -isoButyrylglutaric acid, $\text{COPr}^{\beta}\cdot\text{CH}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, melts at 99° , and crystallises in the monoclinic system [$a:b:c = 1.5927:1:2.5159$; $\beta = 81^{\circ}6'$]. The barium salt contains $2\text{H}_2\text{O}$, and the calcium salt $3\text{H}_2\text{O}$, the silver salt being anhydrous.

[With HARRY SALOMON].—The ketodilactone of β -benzoylglutaric acid,

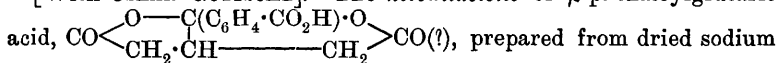


obtained from dried sodium tricarballoylate and benzoic anhydride, melts at 137° , and separates, on adding ether to the chloroform solution, in rhombic crystals [$a:b:c = 0.6478:1:0.8659$]. β -Benzoylglutaric acid, $\text{COPh}\cdot\text{CH}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, crystallising from a mixture of ether and petroleum in bundles of needles, melts at 122° ; the barium salt contains $4\text{H}_2\text{O}$, the calcium and silver salts being anhydrous. Phenylbutyrolactoneacetic acid,



prepared by reducing the dilactone with sodium amalgam, crystallises from water in transparent prisms and melts at 114° ; the barium salt contains $3\text{H}_2\text{O}$, and the calcium salt $2\text{H}_2\text{O}$, the silver salt being anhydrous. Phenylbutyrolactoneacetic acid is hydrolysed only slowly, and the dibasic hydroxy-acid, $\text{C}_{12}\text{H}_{14}\text{O}_5$, could not be isolated; the calcium and barium salts contain $1\text{H}_2\text{O}$, and the silver salt is anhydrous. When dried phenylbutyrolactoneacetic acid is distilled, β -methylphenylisocrotonic acid and β -methylnaphthol are produced.

[With OSKAR GOTTSCHÉ].—The ketodilactone of β -phthaloylglutaric



tricarballoylate and phthalic anhydride, crystallises from chloroform in colourless needles, and melts at 208° . β -Phthaloylglutaric acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, produced by the action of boiling

water on the dilactone, crystallises from ether in small needles, but has no definite melting point, undergoing a change at 135—140°, and finally becoming liquid at the melting point of the dilactone; the *calcium* salt contains 5H₂O, the *barium* salt 9H₂O, and the *silver* salt is anhydrous.

Carboxyphenylbutyrolactoneacetic acid, $\text{CO} \begin{array}{c} \text{O} - \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$ (1),

obtained by reducing the ketodilactone with sodium amalgam, crystallises from boiling water in lustrous plates containing 1H₂O, which is removed at 100°; acetone also deposits it in monoclinic plates, and when anhydrous it melts at 165°. The *calcium* salt contains 2H₂O, and the *barium* salt 6H₂O, the *silver* salt being anhydrous. Hydrolysis with alkalis proceeds slowly, and the dibasic hydroxy-acid, C₁₃H₁₄O₇, has not been isolated; the *barium* and *calcium* salts contain 10H₂O, whilst the *silver* salt is anhydrous.

[With HARRY SALOMON].—The *ketodilactone* of β -acetyltrimethylglutaric acid, $\text{CO} \begin{array}{c} \text{O} - \text{CMe} - \text{O} \\ | \quad | \\ \text{CH}_2 \cdot \text{CMe} \cdot \text{CMe}_2 \end{array} \text{CO}$, obtained from dried sodium camphoronate and acetic anhydride, crystallises from chloroform in long needles, and melts at 147·5—148°. β -Acetyltrimethylglutaric acid, CO₂H·CH₂·CMe(COMe)·CMe₂·CO₂H, crystallises from boiling water in prisms, softens at 125°, and melts at 140°; the *barium* salt contains 3½H₂O, the *calcium* salt 2H₂O, and the *silver* salt is anhydrous. The acid resists the action of sodium amalgam. M. O. F.

Syntheses with Ethyl Sodioacetoacetate and the Formation of Rings of Four Carbon Atoms by means of Sodium Ethoxide. By ARTHUR MICHAEL (*Ber.*, 1900, 33, 3731—3769).—The ester of a substituted malonic acid was mixed with a solution of sodium in absolute alcohol, and the ester of an unsaturated acid was added; the whole was sometimes warmed to complete the reaction. The alcohol was distilled off, the residue dissolved in ether, and substances of an acid nature removed by shaking with dilute aqueous potassium hydroxide; of these acid substances, a part could be set free by saturating the alkaline liquid with carbon dioxide. The neutral product of the reaction was thus obtained pure; other observers (Auwers, *Abstr.*, 1891, i, 546; 1892, i, 41; Ruhemann and Cunningham, *Trans.*, 1898, 73, 1006) have omitted the extraction of the acid products, and obtained only mixtures of different substances.

Ethyl ethylmalonate and fumarate give ethyl pentane- $\alpha\beta\gamma\gamma$ -tetracarboxylate, CO₂Et·CH₂·CH(CO₂Et)·CET(CO₂Et)₂, which boils at 197° (corr.) under 13·5 mm. pressure; the ethyltricarballic acid obtained from it by hydrolysis melts at 155—157°. Of the acid products, one is soluble in aqueous alkali carbonate, and appears to be the triethyl hydrogen ester, for at 180° it loses carbon dioxide and forms a liquid that boils at 168—169° under 11 mm. pressure and has the composition of ethyl pentane- $\alpha\beta\gamma$ -tricarboxylate. Sodium dissolves in an ethereal solution of the tetrethyl salt, and when the product is freed from ether and heated with methyl iodide at 100°, ethyl α -methylpentane- $\alpha\beta\gamma\gamma$ -tetracarboxylate is obtained; this boils at 201—202° (corr.) under 12 mm. pressure, is acted on further by sodium in ethereal solution.

and when hydrolysed with boiling, dilute hydrochloric acid, yields a product melting at 138—146° after several recrystallisations, presumably a mixture of stereoisomeric methylethyltricarballic acids.

Ethyl methylmalonate and fumarate give ethyl butane- $\alpha\beta\gamma$ -tetracarboxylate. This boils at 206.5—207° (corr.) under 20 mm. pressure; when hydrolysed, it yields only β -methyltricarballic acid melting at 143—146°, and not a mixture of stereoisomerides. Sodium acts on it, and the product reacts at 100° with methyl iodide to form ethyl α -methylbutane- $\alpha\beta\gamma$ -tetracarboxylate; this boils at 198—199° under 13 mm. pressure, reacts further with sodium, and can be hydrolysed, although with difficulty, to α -methylbutane- $\alpha\beta$ -tricarboxylic acid, which melts at 190—193°; probably a little of the stereoisomeric acid is formed at the same time.

Ethyl malonate and citraconate give ethyl β -methylpropane- $\alpha\beta\gamma$ -tetracarboxylate. This boils at 199—199.5° (corr.) under 11 mm. pressure, and can be hydrolysed, although with difficulty, to β -methyltricarballic acid melting at 168—173°. From its sodium derivative and methyl iodide, ethyl β -methylbutane- $\alpha\beta\gamma$ -tetracarboxylate can be obtained; this boils at 202—205° (corr.) under 13 mm. pressure, is attacked slowly by sodium, and can be hydrolysed, although with difficulty, to a mixture of stereoisomeric β -methylbutane- $\alpha\beta$ -tricarboxylic acids, from which a product melting at 196—198° was obtained by repeated recrystallisation. By using ethyl instead of methyl iodide, ethyl β -methylpentane- $\alpha\beta\gamma$ -tetracarboxylate is obtained; this boils at 199—200° (corr.) under 10 mm. pressure, can be hydrolysed slowly, and reacts further with sodium. When the sodium derivative of ethyl β -methylpropane- $\alpha\beta\gamma$ -tetracarboxylate is treated with water, the solution freed from neutral substances by extraction with ether, and saturated with carbon dioxide, ethyl methylketotetramethylenetricarboxylate is formed; the sodium derivative of ethyl β -methylpentane- $\alpha\beta\gamma$ -tetracarboxylate yields an analogous ketotetramethylene derivative (see below).

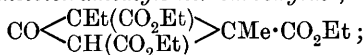
Ethyl methylmalonate and crotonate give β -methylbutane- $\alpha\gamma$ -tricarboxylate; this boils at 160.5—161° (corr.) under 10 mm. pressure, and reacts readily with sodium; the product of this reaction, when heated with methyl iodide, yields ethyl dimethylbutane- $\alpha\gamma$ -tricarboxylate, boiling at 161—162° (corr.) under 9 mm. pressure.

Ethyl malonate and crotonate give ethyl β -methylpropane- $\alpha\gamma$ -tricarboxylate, boiling at 165—166° (corr.) under 11 mm. pressure, together with a little ethyl $\beta\delta$ -dimethylpentane- $\alpha\gamma\gamma$ -tetracarboxylate, boiling and decomposing slightly at 204—207° (corr.) under 9 mm. pressure; the second product must have resulted from the condensation of the first with ethyl crotonate. The sodium derivative of ethyl β -methylpropane- $\alpha\gamma$ -tricarboxylate reacts with methyl iodide; the resulting methyl derivative boils at 166—167° (corr.) under 10 mm. pressure, and reacts only slowly with sodium; it is not identical with the ethyl β -methylbutane- $\alpha\gamma$ -tricarboxylate described above.

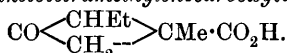
Ethyl propane- $\alpha\beta\beta$ -tricarboxylate (from ethyl ethenyltricarboxylate, sodium ethoxide, and methyl iodide) appears to form a little of a sodium derivative, but only with great difficulty.

Ethyl ethylmalonate and citraconate yield hardly any of the normal

condensation product. The chief product is soluble in alkali hydroxides, but is liberated by saturation with carbon dioxide; it boils at 204—205° (corr.) under 13 mm. pressure, and yields an *oxime*, *phenylhydrazone* and *semicarbazone*, all oily in consistency. It was identified as *ethyl methylethylketotetramethylenetricarboxylate*,



it is hydrolysed readily by boiling dilute hydrochloric acid to a mixture of isomeric *methylethylketotetramethylenecarboxylic acids*,



Of these, the one which is less soluble in water melts at 72—74°; its *silver* salt and *semicarbazone* (melting at 193—194°) were analysed; the more soluble one melts at 37—39°, its *semicarbazone* at 191—192°; when distilled (at 180—182° under 15 mm. pressure) or heated in aqueous solution, it undergoes a partial transformation into the less soluble isomeride.

Ethyl methylmalonate and citraconate yield *ethyl dimethylketotetramethylenetricarboxylate*, boiling at 207—208° (corr.) under 20 mm. pressure. When hydrolysed, this yields a mixture of isomeric *dimethylketotetramethylenecarboxylic acids*, which boils at 187° (corr.) under 25 mm. pressure, and melts at 56—59°; the *semicarbazone* melts at 195—196°.

Ethyl malonate and citraconate yield, in addition to the product described above, *ethyl methylketotetramethylenetricarboxylate*, boiling at 213—214° (corr.) under 17 mm. pressure. When hydrolysed, this yields a single *methylketotetramethylenecarboxylic acid*, melting at 62—64°; the *semicarbazone* melts at 192—193°.

When ethyl cinnamate in ethereal solution is digested with sodium until the latter has dissolved, the product poured into water, and the aqueous solution extracted with ether, an oil boiling at 205—210° under 15—17 mm. pressure is obtained, probably a product of polymerisation. From ethyl crotonate, a product was obtained boiling at 126° (corr.) under 9 mm., at 258—259° under 773 mm. pressure. It has a composition and vapour density corresponding to a bimolecular polymeride of the ester, $\text{C}_{12}\text{H}_{20}\text{O}_4$. When hydrolysed, it yields a dibasic acid, $\text{C}_8\text{H}_{12}\text{O}_4$, which melts at 128—129°, and is oxidised almost instantly by permanganate; its *silver* and *barium* salts, the latter with $1\text{H}_2\text{O}$, were prepared and analysed.

In an introduction to the paper, the mechanism of the reactions described is considered from the point of view occupied by the author (Abstr., 1900, i, 321). C. F. B.

Action of Formaldehyde Solution on Calcium Carbide. By LUDWIG VANINO (*Chem. Centr.*, 1900, ii, 1150; from *Pharm. Centr.-H.*, 1900, 41, 666).—Formaldehyde may be used to moderate the action of water on calcium carbide. With a solution of formalin in 8 vols. of water, the rate of evolution of acetylene is much slower than with water, whilst in 40 per cent. solution the aldehyde almost completely inhibits the action. E. W. W.

Specific Difference between Ketones and Aldehydes. By WILLIAM OECHSNER DE CONINCK and SERVANT (*Bull. Acad. Roy. Belg.*, 1900, 313—316).—Whereas ketones, either alone or in presence of water or dilute alkali, are not changed at the ordinary temperature by the long-continued passage through them of a current of air, aldehydes under the same conditions are sensibly oxidised to acids; the experiments were made with acetone, benzophenone, and acetaldehyde.
W. A. D.

Methyl Ethyl Ketone. By LÉON VAN REYMEANT (*Bull. Soc. Roy. Belg.*, 1900, 724—744).—The product of the action of chlorine (1 mol.), or of sulphuryl chloride on methyl ethyl ketone, consists, two-thirds of the secondary chloro-derivative, $\text{COMe}\cdot\text{CHMeCl}$ (Vladesco, *Abstr.*, 1892, 424, 810), and nearly one-third of *chloromethyl ethyl ketone*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\text{Me}$. The former boils at 115° under 758 mm. pressure, has a sp. gr. 1.032 at 0° , and, on oxidation, yields α -chloropropionic acid; the latter boils at 125° under 756 mm. pressure, has a sp. gr. 1.08 at 13° , n_D 1.42701 at 10° , a mol. refraction 25.35 (calc. 25.55), and yields enloroacetic acid on oxidation. With bromine, similar derivatives, $\text{COMe}\cdot\text{CHMeBr}$ and $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CH}_2\text{Me}$, are obtained, the former boiling at 133 — 134° , and the latter at 145 — 146° ; both are nearly colourless, tear-exciting liquids, which become coloured in the light. β -Acetylmethyl acetate, $\text{CH}_3\cdot\text{CO}_2\cdot\text{CHMeAc}$, obtained by boiling the foregoing secondary chloro-derivative with alcoholic potassium acetate, boils at 164° under the ordinary pressure, has a sp. gr. 1.027 at 13° , n_D 1.4143 at 13.5° , and a mol. refraction 31.62 (calc. 31.61); *propionylmethyl acetate*, $\text{CH}_3\cdot\text{CO}_2\cdot\text{CH}_2\text{COEt}$, corresponding with the primary chloro-derivative, boils at 176° , and has a sp. gr. 1.029 at 13.4° , n_D 1.4151, and a mol. refraction 31.37 (calc. 31.37). *Methylacetylcarbinol*, $\text{CHMeAc}\cdot\text{OH}$, obtained by hydrolysing either the corresponding chloro-derivative or acetate, melts at 15° , boils at 148° , and has a sp. gr. 1.012 at 16.5° , n_D 1.4272, and a mol. refraction 22.20 (calc. 23.32). *Propionylcarbinol*, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\text{Me}$, boils at 160° .

Although cyanoacetone, $\text{CH}_2\text{Ac}\cdot\text{CN}$, cannot be obtained by the interaction of chloroacetone with potassium cyanide, the latter readily converts the foregoing halogen derivatives of methyl ethyl ketone into their cyanides at the ordinary temperature. α -Acetylpropionitrile, $\text{CHMeAc}\cdot\text{CN}$, boils at 145 — 146° (Vladesco, *loc. cit.*, gives 156°), has a sp. gr. 1.494 at 13° , and a mol. refraction 25.03 (calc. 25.33); with sodium ethoxide, it forms a *sodium* derivative, $\text{CNaMeAc}\cdot\text{CN}$, which, with methyl iodide, yields *dimethylacetylacetoneitrile*, $\text{CMe}_2\text{Ac}\cdot\text{CN}$, a yellow liquid which boils at 163 — 164° , and has a sp. gr. 1.008 at 13° . The sodium derivative reacts with chlorine, forming α -chloro- α -acetylpropionitrile, $\text{CClMeAc}\cdot\text{CN}$, a yellowish liquid boiling at 95° under 45 mm. pressure; the analogous bromo-derivative, $\text{CBrMeAc}\cdot\text{CN}$, boils at 122° under 30 mm. pressure. Both these compounds react energetically with potassium cyanide to form *methylacetylmalononitrile*, $\text{CMeAc}(\text{CN})_2$, which boils at 195° .

α -Acetylpropionic acid, $\text{CHMeAc}\cdot\text{CO}_2\text{H}$, obtained by hydrolysing its

nitrile, boils at 224° under 34 mm. pressure. *α*-Chloro-*α*-acetylpropionic acid, $\text{CClMeAc}\cdot\text{CO}_2\text{H}$, boils at 141° under 45 mm. pressure, and *α*-bromo-*α*-acetylpropionic acid, $\text{CBrMeAc}\cdot\text{CO}_2\text{H}$, at 150° under the same pressure.

Propionylacetonitrile, $\text{COEt}\cdot\text{CH}_2\cdot\text{CN}$, obtained from the corresponding chloro-derivative, boils at 164°, has a sp. gr. 0.976 at 9° and a mol. refraction 25.00 (calc. 27.03).
W. A. D.

Derivatives of Methyl Nonyl Ketone. By HENRI CARETTE (*Compt. rend.*, 1900, 131, 1225—1227).—Methyl nonyl ketone and benzaldehyde do not interact even at 120° unless they are mixed together in the presence of potassium hydroxide. The compound, $\text{C}_{18}\text{H}_{26}\text{O}$, produced when a cold 0.25 per cent. solution of the alkali in dilute alcohol is added to a mixture of the ketone and aldehyde in mol. proportions, readily dissolves in the ordinary organic solvents, melts at 41—42°, and boils at 245° under 35 mm. pressure. The *polymeride*, $(\text{C}_{18}\text{H}_{26}\text{O})_2$, obtained either by boiling the preceding compound with a 1 per cent. solution of potassium hydroxide in 95 per cent. alcohol, or by heating its generators in the same medium, crystallises in needles, melts at 116°, and boils with partial decomposition at 310—340° under 35 mm. pressure.
G. T. M.

Birotation of Dextrose. By YUKICHI OSAKA (*Zeit. physikal. Chem.*, 1900, 35, 661—706).—The change of rotation of dextrose takes place in accordance with the equation $k = 1/t \cdot \log_e(a_0 - a_\infty)/(a - a_\infty)$, where a_0 and a_∞ are the initial and final rotations, and a is the rotation at the time t . This has been proved by Levy (*Abstr.*, 1895, i, 586) and Trey (*Abstr.*, 1896, ii, 139; 1897, ii, 299), and the author now finds, using numbers obtained by Tollens and others, that the same law holds in the case of lævulose, rhamnose, *l*-arabinose, fucose, *l*-xylose, *d*-galactose, maltose, and milk sugar. In the case of dextrose, the change of rotation is accelerated in the presence both of hydroxyl and hydrogen ions, the catalytic effect of the former, however, being much greater than that of the latter. The velocity of the retrogression of the rotation is approximately proportional to the concentration of the hydroxyl ions, and to the square root of the concentration of the hydrogen ions. Neutral salts appear to increase the catalytic efficiency of the hydroxyl ions, but to be practically without effect on that of the hydrogen ions. The author agrees with Cohen (*Abstr.*, 1900, ii, 716) in regarding dextrose as a very weak acid.
J. C. P.

Influence of the Nature and Intensity of Light on the Inversion of Sucrose by Mineral Acids. By HENRI GILLOT (*Bull. Acad. Roy. Belg.*, 1900, 863—874).—The author has examined comparatively the rate of inversion of sucrose in aqueous solution containing sulphuric or hydrochloric acid, when exposed to light of different wave-lengths; in each case, the fall of rotatory power and the increase of cupric-reducing power were compared with similar values obtained with a solution left in darkness. Light of all wave-lengths promotes inversion, but rays in the blue, violet, and ultra-violet are much more active than those in the yellow or red.
W. A. D.

Behaviour of Sucrose Solutions towards Strontia at 125—128°. By A. SCHÖNE and BERNHARD TOLLENS (*Zeit. Ver. deut. Zucker-Ind.*, 1900, 978—979).—When aqueous solutions of sucrose and strontium hydroxide are heated together in an autoclave at 125—128°, no trace of raffinose is formed. The raffinose present in molasses hence comes from the beet. T. H. P.

Diagnosis of Primary and Secondary Amines. By OSCAR HINSBERG (*Ber.*, 1900, 33, 3526—3529. Compare Abstr., 1891, 49).—Solonina (*J. Russ. Phys. Chem. Soc.*, 1897, 29, 404; Abstr., 1900, i, 147) and Bamberger (Abstr., 1899, i, 701) have shown that benzene- or toluene-sulphonic chloride cannot always be used with success in the diagnosis of primary and secondary amines. The author now recommends β -anthraquinonesulphonic chloride in the presence of excess of alkali (MacHoul, Abstr., 1881, 51). The amide thus obtained, if discoloured, is recrystallised and then 0.05 gram dissolved in hot alcohol, and to the colourless, or only pale yellow, solution, 0.5 c.c. of 25 per cent. potassium hydroxide is added. If a secondary amine were originally present, the colour remains unaltered, and on addition of more alkali, the sulphonamide is precipitated in a crystalline form; with a primary amine, however, the solution assumes a deep yellow or yellowish-red colour owing to the formation of a salt. The method has been tried with a number of bases and has given very satisfactory results.

β -Anthraquinonesulphone-n-heptylamide, $C_{14}H_7O_2 \cdot SO_2 \cdot NH \cdot C_7H_{15}$, forms yellow needles melting at 160° and insoluble in water.

β -Anthraquinonesulphonemethylanilide, $C_{14}H_7O_2 \cdot SO_2 \cdot NMePh$, forms pale yellow needles melting at 182°. J. J. S.

Alternation of Volatility in the Series of Normal Primary Diamines. By LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1900, 795—803).—In the series of normal primary monoamines, $NH_2 \cdot CH_2 \cdot [CH_2]_n \cdot CH_3$, there is a regular progressive increase in the boiling point of about 27°, the difference between the boiling points of the even pair, C_2 and C_4 (57°), being practically the same as that of the odd pair, C_3 and C_5 (54°). In the case of the diamines, $NH_2 \cdot [CH_2]_n \cdot NH_2$, however, there is an alternation in boiling point similar to that traced in the case of the acid chlorides (Abstr., 1899, i, 735), the successive differences in boiling point of the C_2 , C_3 , C_4 , and C_5 diamines being 19°, 25°, and 19°. The difference between the even pair, C_2 and C_4 (44°), is, however, the same as that between the odd pair, C_3 and C_5 (44°). Similar relationships connect the boiling points of the two classes of amines and those of the parent hydrocarbons; for these, the original should be consulted. W. A. D.

Action of α -Chlorohydrin on some Tertiary Amines. By ALEXANDER BIENENTHAL (*Ber.*, 1900, 33, 3500—3506).—The additive compound, $NEt_3Cl \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, formed on heating α -chlorohydrin with triethylamine for 8 hours at 100°, is a non-crystallisable syrup which, when treated with moist silver hydroxide in aqueous solution, yields a strongly caustic base; the picrate of the

latter forms long prisms melting at 114° , and the *platinichloride* monoclinic plates melting at 215.5° .

The *additive* compound, $\text{NPr}_3\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH} \cdot \text{OH}$, of tripropylamine, obtained similarly, is also a syrup; the *picrate* of the *base*, $\text{OH} \cdot \text{NPr}_3 \cdot \text{C}_3\text{H}_7\text{O}_2$, crystallises from alcohol in small, yellow prisms, and melts at $79-80^{\circ}$, the *aurichloride* melting at $94-95^{\circ}$.

The *compound*, $\text{C}_5\text{NH}_{10}\text{MeCl} \cdot \text{C}_3\text{H}_7\text{O}_2$, formed by the interaction of 1-methylpiperidine and α -chlorohydrin at 100° , crystallises from alcohol in long prisms, sinters at 229° and melts at $233-234^{\circ}$; the *platinichloride* of the derived *base* crystallises from alcohol in thick, yellow prisms, and decomposes at $206-207^{\circ}$, the crystalline *mercurichloride* melting at $169-170^{\circ}$.

The *compound*, $\text{C}_9\text{NH}_7\text{Cl} \cdot \text{C}_3\text{H}_7\text{O}_2$, derived from quinoline, crystallises from alcohol in small, white leaflets, melts at 170° , and, with moist silver oxide, yields a *base* the *platinichloride* of which forms small, yellow plates melting at $282-283^{\circ}$; the *aurichloride* is amorphous and melts at $100-101^{\circ}$, the *mercurichloride* forms transparent, white needles melting at $114-115^{\circ}$, and the *picrate* melts at 120° .

The *strychnine* derivative, $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2\text{Cl} \cdot \text{C}_3\text{H}_7\text{O}_2$, formed on heating the components for 1 hour at 190° , crystallises from alcohol in white prisms, and does not melt at 290° ; it is not acted on by alkalis, but with moist silver oxide yields a *base* the *platinichloride* of which crystallises from alcohol in small, yellow needles melting at 230° ; the *aurichloride* melts at 214° , and the *mercurichloride* at 199° , whilst the *picrate* decomposes at 280° .

No well-characterised derivative could be obtained by the interaction of 2-picoline with α chlorohydrin. W. A. D.

Conversion of Amino-fatty Acids into the Corresponding Chloro-acids. By EMIL JOCHEM (*Zeit. physiol. Chem.*, 1900, 31, 119—131. Compare Curtius, *Abstr.*, 1884, 42; Tilden, *Trans.*, 1895, 67, 489).—Chlorinated acids are readily obtained when 1 mol. proportion of sodium nitrite in concentrated solution is added drop by drop to the amino-acid dissolved or suspended in 10 times its weight of concentrated hydrochloric acid. The method has given good results with amino-derivatives of the acetic and oxalic acid series, also with aromatic-amino acids which contain the amino-group in a side chain, but not when the amino-group is directly attached to the benzene nucleus, or yet with fatty or aromatic amines.

This reaction accounts for the formation of chloro-acids when albumin is treated with hydrochloric acid and sodium nitrite.

α -Chloroglutaric acid, $\text{C}_5\text{H}_7\text{O}_4\text{Cl}$, crystallises from a mixture of ether and light petroleum in well developed pyramids, sinters at 97° , and is completely melted at 100° ; it dissolves readily in most solvents, with the exception of benzene, chloroform, or light petroleum; aqueous solutions of the acid or of its salts readily decompose, yielding *α -hydroxyglutaric acid*. The *copper* and *barium* salts are both readily soluble in water, but are precipitated on the addition of alcohol; the *diethyl* ester is an oil distilling at $140-145^{\circ}$ under 15 mm. pressure, and has a sp. gr. 1.14 at 23° .

α -Chloroisohexzoic acid, $\text{C}_6\text{H}_{11}\text{O}_2\text{Cl}$, has been obtained from leucine in

the form of an oil insoluble in water, and readily undergoes decomposition, evolving hydrogen chloride even at 40° ; its *ethyl* ester distils at 190° under atmospheric, or at $91\text{--}95^{\circ}$ under 15 mm., pressure, and has a sp. gr. 1.01 at 23° ; when hydrolysed, it yields an α -hydroxyisohexoic acid melting at $67\text{--}70^{\circ}$, the zinc salt of which contains $2\text{H}_2\text{O}$ (compare Waage, *Annalen*, 1861, 118, 87; Gmelin, *Abstr.*, 1894, i, 501).
J. J. S.

Action of Pyruvic Acid on its Ammonium Salt. By A. W. K. DE JONG (*Rec. Trav. Chim.*, 1900, 19, 259—310).—The pyruvic acid employed was prepared by a modification of the methods devised by Visser (here described for the first time) and Simon, namely, by heating together potassium hydrogen tartrate, potassium hydrogen sulphate, and sulphuric acid. The estimation of the acid is effected by means of its phenylhydrazone, and the corrections necessary for the solubility of the compound are given.

When solid ammonium carbonate is gradually added to a concentrated solution of pyruvic acid, a considerable elevation of temperature occurs, carbon dioxide is evolved, and *ammonium α -acetylaminopropionate* slowly crystallises out. Estimation of the amount of carbon dioxide evolved shows that for each mol. of the latter a mol. of ammonia enters into reaction. The free acid is obtained by adding to pyruvic acid half the quantity of ammonium carbonate required for neutralisation, or by treating the ammonium salt with an equivalent quantity of pyruvic acid. α -Acetylaminopropionic acid, $\text{NHAc}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, crystallises in large, rhombic plates or needles [$a:b:c = 0.7729:1:1.0983$], melts at $132\text{--}133^{\circ}$, and is soluble in water or alcohol but almost insoluble in ether. When heated with hydrochloric acid or sodium hydroxide solution, it is hydrolysed to acetic acid and α -alanine. Conversely, α -acetylaminopropionic acid is readily obtained by heating α -alanine with a slight excess of acetic anhydride at about 70° . The following metallic salts of α -acetylaminopropionic acid have been prepared; the sodium and potassium salts could only be obtained as hygroscopic syrups, the others are crystalline: ammonium with H_2O , barium with $1\frac{1}{2}\text{H}_2\text{O}$, calcium with $1\frac{1}{2}\text{H}_2\text{O}$, magnesium with $7\text{H}_2\text{O}$, zinc with H_2O , lead with $3\text{H}_2\text{O}$, copper, and silver with H_2O .

Ethyl α -acetylaminopropionate crystallises in hygroscopic needles melting at $39\text{--}40^{\circ}$, and by the action of chlorine is converted into the corresponding *chloroethyl* ester, $\text{C}_5\text{H}_8\text{O}_3\text{N}\cdot\text{CHClMe}$, which, on hydrolysis, yields hydrogen chloride, acetaldehyde, and α -acetylaminopropionic acid. The *amide*, $\text{C}_5\text{H}_8\text{O}_3\text{N}\cdot\text{NH}_2$, crystallises in small, rhombic prisms melting at $157\text{--}158^{\circ}$.

α -Acetylaminopropionic acid also forms salts with acids. The *hydrochloride*, $\text{C}_5\text{H}_8\text{O}_3\text{N}\cdot\text{HCl}$, crystallises in hygroscopic needles and is unstable. The *nitrate* crystallises in very soluble needles melting and decomposing at $64\text{--}65^{\circ}$. When neutralised with calcium carbonate, the well-crystallised double salt, $(\text{C}_5\text{H}_8\text{O}_3\text{N})_2\text{Ca}\cdot(\text{NO}_3)_2\text{Ca}\cdot 6\text{H}_2\text{O}$, is formed.

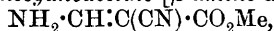
Ammonium pyruvate, when pure, forms white needles. As an explanation of the formation of α -acetylaminopropionic acid, it is suggested that ammonium pyruvate is tautomeric with the as yet

unknown α -aminohydroxypropionic acid. On this hypothesis, the reactions concerned in the formation of α -acetylaminopropionic acid are brought into harmony with the views generally held as to the action of ammonia on aldehydes and ketones.

From the mother liquors obtained in the preparation of α -acetylaminopropionic acid, two new acids of the composition $C_6H_{11}O_5N$ have been isolated by means of their barium salts. The one crystallises in needles decomposing at 220° , whilst the other crystallises, with $1H_2O$, in small prisms which decompose at 208° . The barium and silver salts of these acids have been prepared and analysed. N. L.

Action of Ammonia and Aniline on Hydroxymethylene-cyanoacetic Esters and their Alkyl Derivatives. By E. GRÉGOIRE DE BOLLEMONT (*Bull. Soc. Chim.*, 1901, [iii], 25, 39—46).—The alkyl hydroxy-, methoxy-, and ethoxy-cyanoacrylates (this vol., i, 116), when treated with ammonia, yield one and the same series of amino-derivatives, $NH_2 \cdot CH : C(CN) \cdot CO_2R$. These are stable, crystalline compounds which are very slightly soluble in water, but soluble in alcohol, ether, or excess of ammonia; their solutions are neutral, and give no coloration with ferric chloride.

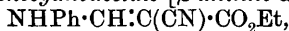
Methyl aminomethylenecyanoacetate [β -amino- α -cyanoacrylate],



crystallises in long, colourless needles melting at 128° . The *ethyl* ester crystallises in slender needles melting at 130° and boiling at 216° under 19 mm. pressure. The *propyl* ester crystallises in small prisms melting at 46° , and the *amyl* ester in large, white scales melting at 101° .

The following anilino-derivatives are precisely analogous to these amino-derivatives.

Ethyl anilinomethylenecyanoacetate [β -anilino- α -cyanoacrylate],



crystallises from alcohol in long needles or thin, monoclinic plates, according to the temperature and concentration. The *methyl* ester crystallises in slender, white needles melting at 175° , the *propyl* ester in large tablets melting at 89 — 90° , and the *amyl* ester in white scales melting at 90° . N. L.

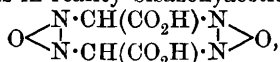
Constitution of Nitroferricyanides. By ARTURO MIOLATI (*Zeit. anorg. Chem.*, 1900, 25, 318).—A question of priority (compare Hofmann, *Abstr.*, 1900, i, 591). E. C. R.

Physico-chemical Researches on the Behaviour of Uric Acid and its Salts in Solution. By WILHELM HIS, jun., and THEODOR PAUL (*Zeit. physiol. Chem.*, 1900, 31, 1—42, and 64—78. Compare *Abstr.*, 1900, i, 591).—The authors review previous work on the solubility of uric acid, and they find that 1 part of the acid is soluble in 39,480 parts of water at 18° . When the finely divided acid is shaken with water at 18° , a saturated solution is obtained in an hour; it is not permissible to cool a solution saturated at a high temperature, on account of decomposition of the uric acid. The molecular conductivity of a saturated uric acid solution is 32.24 at 18° , when allowance has

been made for the conductivity of the solvent water. Indirectly, by work on sodium and potassium urate solutions, it is found that the molecular conductivity of uric acid for infinite dilution is 339 at 18°. Hence, in a saturated uric acid solution, 9·5 per cent. of the acid is electrolytically dissociated. Further, the affinity constant has the value 0·00000151. The authors confirm the observation made by other workers, that uric acid is decomposed on prolonged contact with water, this leading to an increased solubility. A saturated solution of uric acid in contact with platinised electrodes is more rapidly decomposed, and its conductivity diminishes.

As regards the solubility of uric acid in solutions of mineral acids, theory requires a repression of the dissociation and consequent diminution of the solubility. This conclusion is borne out both qualitatively and quantitatively by experiment: 1 part of uric acid dissolves in 42,430 parts of *N*-hydrochloric acid and in 44,140 parts of *N*-sulphuric acid. Even in more concentrated acid solutions, the solubility is less than in pure water, whence it follows that uric acid cannot act as a base. The tendency of uric acid to decompose when in contact with water practically disappears in the presence of mineral acids. The estimation of uric acid in urates by precipitation with excess of hydrochloric, or, better, sulphuric acid is an exact process; a correction of 2 mg. for each 100 c.c. of liquid at 18° should be applied. J. C. P.

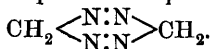
Bisazoxyacetic Acid, Bisazoxymethane, and Hydraziaacetic Acid. By ARTHUR HANTZSCH and MARTIN LEHMANN (*Ber.*, 1900, **33**, 3668—3685).—The substance described by Curtius (*Abstr.*, 1889, 369) as triazoxyacetic acid is in reality bisazoxyacetic acid,



and is best prepared by exposing powdered bisdiazooacetic acid to the gas evolved from nitric acid and arsenious oxide, although it is also formed by the action of bromine vapour and chlorine on the acid. It is a purple-red powder, which forms a carmine-red solution in water, and decomposes at 148° evolving purple vapours of bisazoxymethane. It is quantitatively reduced in aqueous solution at 0° by hydrogen sulphide to bisdiazooacetic acid. The aqueous solution of the acid rapidly decomposes and becomes colourless, hydraziaacetic acid being formed. The solution in 1 mol. of sodium hydroxide also rapidly decomposes, whilst the solution of the normal sodium salt is quite stable. This salt, $\text{C}_2\text{H}_2\text{O}_2\text{N}_4(\text{CO}_2\text{Na})_2$, crystallises in flat, hygroscopic, red plates. The *barium* salt is a heavy, orange-yellow, microcrystalline powder, and the *silver* salt is a dark green powder which explodes very violently at 210°. The silver salt reacts with alkyl iodides, but the resulting esters could only be obtained in the form of impure, viscid oils.

Bisazoxymethane, $\text{O} \begin{array}{c} \diagup \text{N} \cdot \text{CH}_2 \cdot \text{N} \diagdown \\ \diagdown \text{N} \cdot \text{CH}_2 \cdot \text{N} \diagup \end{array} \text{O}$, is formed in very small amount (1—2 per cent. of that calculated) when bisazoxyacetic acid is gently heated, carbon dioxide being at the same time formed and a residue of impure bisdiazomethane left. It is obtained pure by sublimation, in delicate, purple-red needles often 1 centimetre in length, and when

quickly heated melts at 75°. It dissolves in water and many organic solvents, and decomposes when preserved. In benzene solution, the molecular weight determined by the cryoscopic method agrees with that required for the formula just given. On reduction with hydrogen sulphide in aqueous solution, it is converted into bisdiazomethane,



Hydraziacetic acid, $\begin{array}{c} \text{NH} \\ | \\ \text{NH} \end{array} > \text{CH} \cdot \text{CO}_2\text{H}$, is formed from bisazoxyacetic acid according to the equation $\text{C}_4\text{H}_4\text{O}_6\text{N}_4 = \text{C}_2\text{H}_4\text{O}_2\text{N}_2 + 2\text{CO}_2 + \text{N}_2$, when the aqueous solution of the latter is allowed to decompose at 25–30°. It is a very sparingly soluble, crystalline powder, and decomposes at 190°. It has a conductivity μ 73 (at 25° and v 32), and is, therefore, as strong an acid as monochloroacetic acid, and forms stable soluble salts. The *methyl* ester, prepared from the silver salt, crystallises in small needles melting at 102°, and has the calculated molecular weight in benzene solution. It is readily soluble in water, and when treated in this solution with mercuric oxide yields methyl diazoacetate. Hydraziacetic acid decomposes when its solution is boiled, or when it is treated with acids, into hydrazine and glyoxylic acid, and the latter then undergoes a secondary reaction, yielding oxalic and glycollic acids. Both bisdiazooacetic acid and bisazoxyacetic acid are converted by alkaline reduction into hydraziacetic acid. A. H.

New Reactions of Organometallic Derivatives. By EDMOND E. BLAISE (*Compt. rend.*, 1901, 132, 38–41).—The author has investigated the reactions between nitriles, alkyl haloids, alkyl salts of the α -bromo-acids of the acetic series, and alkylcarbimides in presence of magnesium bromide or iodide, or zinc bromide. In the case of nitriles, the reaction is $\text{R} \cdot \text{C} \cdot \text{N} + \text{MgBrR}' = \text{RR}'\text{C} \cdot \text{N} \cdot \text{MgBr}$ and the imino-derivatives thus obtained yield ketones, $\text{R} \cdot \text{CO} \cdot \text{R}'$, on treatment with dilute acids. The condensation of nitriles of the benzene series with alkyl iodides in presence of magnesium yields new ketones and also the corresponding semicarbazones, the *o*-nitriles reacting less readily than the *p*-nitriles. Nitriles of the acetic series likewise yield ketones when treated with the organo-metallic derivatives.

With the alkyl salts of α -bromo-acids of the acetic series the reaction is $\text{R} \cdot \text{CN} + \text{Zn} + \text{CR}'\text{HBr} \cdot \text{CO}_2\text{Et} = \text{ZnBr} \cdot \text{N} \cdot \text{CR} \cdot \text{CHR}' \cdot \text{CO}_2\text{Et}$, and the products yield alkyl salts of the β -ketonic acids, $\text{R} \cdot \text{CO} \cdot \text{CHR}' \cdot \text{CO}_2\text{Et}$. This method is of very general application, since the radicles may be varied in both the nitrile and the bromo-acid. With ethyl bromoacetate, however, the condensation goes further, but this difficulty is got over by condensing ethyl cyanoacetate with alkyl iodides in presence of magnesium, $\text{CN} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} + \text{EtMgI} = \text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CEt} \cdot \text{N} \cdot \text{MgI}$ and, subsequently, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{COEt}$. No other general method admits of the preparation of the alkyl salts of the acylacetic acids.

With dinitriles, the reaction is $\text{CN} \cdot \text{CN} + \text{EtMgI} = \text{CN} \cdot \text{CEt} \cdot \text{N} \cdot \text{MgI}$ and $\text{CN} \cdot \text{CEt} \cdot \text{N} \cdot \text{MgI} + \text{EtMgI} = \text{MgI} \cdot \text{CN} + \text{CEt}_2 \cdot \text{N} \cdot \text{MgI}$, a ketone being obtained from this product in the usual way. With carbimides, the reaction is $\text{NPh} \cdot \text{C} \cdot \text{O} + \text{RMgI} = \text{NPh} \cdot \text{CR} \cdot \text{O} \cdot \text{MgI}$ and subsequently $\text{NPh} \cdot \text{CR} \cdot \text{OH}$ and $\text{NHPh} \cdot \text{CO} \cdot \text{R}$. Other similar reactions are under

investigation. Caprylene, hexylene, and phenylacetylene do not condense with organo-metallic derivatives under the usual conditions.

C. H. B.

Electrolytic Oxidation of Toluene. By AARON MERZBACHER and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1900, 22, 723—725).—The electrolytic oxidation of toluene has already been attempted (see James, Abstr., 1899, i, 909). The authors have varied the conditions and succeeded in obtaining a small quantity of benzaldehyde and ethyl benzoate at the anode. The anode liquid was an alcoholic solution of toluene, and the cathode liquid was a sulphuric acid solution. Similar results have been obtained with ethylbenzene in place of toluene.

J. C. P.

Phenyl-*p*-nitro-*o*-tolylsulphone and some of its Derivatives. By R. S. NORRIS (*Amer. Chem. J.*, 1900, 24, 469—491).—*p*-Nitro-*o*-toluenesulphonic chloride crystallises in large, yellow rhombs, and melts at 44°. When this compound is heated with benzene in presence of aluminium chloride, *phenyl-p-nitro-o-tolylsulphone*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_2\text{Ph}$, is obtained which crystallises from hot alcohol in thin plates, melts at 158°, and is easily soluble in benzene, acetone, or hot light petroleum. The sulphone dissolves in concentrated sulphuric and nitric acids and is reprecipitated on dilution with water; when treated with fuming sulphuric acid, it is converted into a sulphonic acid, $\text{C}_{13}\text{H}_{11}\text{O}_7\text{NS}_2$, the *barium* salt of which was prepared and analysed. Sodium and potassium hydroxides react with the sulphone with formation of a purple precipitate.

Phenyl-p-amino-o-tolylsulphone, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_2\text{Ph}$, obtained by reducing *phenyl-p-nitro-o-tolylsulphone* with ammonium sulphide, crystallises from alcohol in thin plates, melts at 156°, and dissolves readily in alcohol, acetone, or benzene.

Phenyl-p-nitro-o-tolylsulphone is not attacked by chromic acid, but when treated with aqueous potassium permanganate, it is converted into *p-nitro-o-phenylsulphonebenzoic acid*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{SO}_2\text{Ph}) \cdot \text{CO}_2\text{H}$, which crystallises in white needles, melts at 196°, and is easily soluble in acetone; its *barium* and *calcium* salts are described. This acid is isomeric with the *p*-nitro-*o*-benzoylbenzenesulphonic acid obtained by Hollis (Abstr., 1900, i, 293). Phosphorus pentachloride readily reacts with the acid with production of *p-nitro-o-phenylsulphonebenzoic chloride*, which separates from chloroform in colourless, rhombic crystals, melts at 109°, and dissolves easily in chloroform, ether, benzene, or light petroleum; it is not affected by water at the ordinary temperature, but is readily decomposed by hot water or dilute alkali hydroxides. By the action of dilute ammonia, the chloride is converted into *p-nitro-o-phenylsulphonebenzamide*, which crystallises from chloroform in prisms, melts at 191—192°, and is readily soluble in acetone or hot alcohol. On the addition of aluminium chloride to a warm solution of *p-nitro-o-phenylsulphonebenzoic chloride* in benzene, a brown, tarry mass was obtained which was not further investigated.

With a view to obtaining *p-nitro-o-cyanodiphenylsulphone* which, on hydrolysis, would yield *p-nitro-o-phenylsulphonebenzoic acid*, a

solution of *p*-nitro-*o*-cyanobenzenesulphonic chloride in benzene was heated with aluminium chloride, but only a tarry product was obtained from which *p*-nitro-*o*-cyanodiphenylsulphone could not be isolated. E. G.

Systematisation and Nomenclature of Dicyclic Compounds. By ADOLF VON BAEYER (*Ber.*, 1900, 33, 3771—3775).—The paper constitutes an attempt to systematise the nomenclature of compounds derived from those dicyclic hydrocarbons which contain two or more atoms of carbon common to both rings. M. O. F.

Nitroanthracene. By JACOB MEISENHEIMER (*Ber.*, 1901, 33, 3547—3549).—Liebermann and Lindemann's "nitrosoanthrone," $C_6H_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CH(ONO)} \diagup \end{array} C_6H_4$ (Abstr., 1881, 99) is in reality 10-nitroanthracene, $C_6H_4 \begin{array}{c} \diagup \text{CH} \diagdown \\ \diagdown \text{C(NO}_2\text{)} \diagup \end{array} C_6H_4$, as it is not identical with anthraquinonemmonoxime. On reduction with stannous chloride, it is converted into 10-anthramine, $C_6H_4 \begin{array}{c} \diagup \text{CH} \diagdown \\ \diagdown \text{C(NH}_2\text{)} \diagup \end{array} C_6H_4$, which for complete identification was converted into its *acetyl* derivative, $C_{16}H_{13}ON$. This separates from alcohol in greenish needles melting at 273—274°, and in alcoholic solution shows a beautiful blue fluorescence. A. L.

Compounds of Metallic Salts with Aromatic Amines. By DANIEL TOMBECK (*Ann. Chim. Phys.*, 1900, [vii], 21, 383—419).—This paper contains a detailed account of the preparation and properties of the compounds from metallic salts and organic amines; the majority of these substances have already been described (compare Abstr., 1897, i, 463, 560; 1898, i, 566). Aniline and its homologues form compounds with silver oxy-salts, two mols. of the base combining with one of the metallic sulphate or nitrate. These substances dissolve in cold water without alteration, but decompose when their solutions are warmed, producing silver mirrors on the walls of the containing vessels. Ethylaniline unites with silver nitrate to form a compound of this type, but does not combine with other oxy-salts.

The three anhydrous calcium halogen salts combine with two molecular proportions of aniline, forming deliquescent compounds separating in tabular crystals. G. T. M.

Electrolytic Reduction of Nitro-compounds. By ALBERT ROHDE (*Zeit. Elektrochem.*, 1900, 7, 328—332, and 338—341).—The experiments were made by the method of Elbs (Abstr., 1899, i, 270; this vol., i, 74).

m-Nitrodimethylaniline gives tetramethyl-*m*-diaminoazobenzene; yield 93 per cent. Further reduction yields the hydrazo-compound.

Dimethyl-*m*-nitro-*o*-toluidine, ($Me:NMe_2:NO_2 = 1:2:4$), was prepared by nitration of dimethyl-*o*-toluidine dissolved in a large excess of concentrated sulphuric acid, in the cold, the yield being 91 per cent. of the calculated quantity. The compound is a yellowish oil which, when reduced electrolytically, yields tetramethyl-*m*-diamino-*p*-azotoluene; yield 86 per cent. By recrystallisation from alcohol, it is obtained

in leaflets melting at 99°. Further reduction leads to the hydrazo-compound, which forms colourless crystals melting at 127°. When exposed to the air, this is oxidised to the azo-compound, which, however, appears to be a different modification, since it crystallises in more needle-shaped crystals, and melts at 119°. The hydrazo-compound did not yield a benzidine derivative.

m-Nitromethylaniline gives, on reduction, dimethyl-*m*-diaminoazobenzene, in yield of about 85 per cent. Further reduction gives a solution of the hydrazo-compound, which was not isolated in the solid form.

p-Nitrodimethylaniline gives dimethylamine, and *p*-aminophenol, when reduced in a hot solution in the usual way; in the cold, *p*-aminodimethylaniline is formed. An azo- or hydrazo-compound was not formed in either case. These results are readily explained on the assumption that a phenylhydroxylamine derivative, $\text{OH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, is first formed, which undergoes intermolecular change, yielding a diiminoquinone, $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{OH}$. In the hot liquid, this compound decomposes into dimethylamine and $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}$, from which *p*-aminophenol is derived, whereas in the cold solution it is reduced without decomposition to *p*-aminodimethylaniline.

Benzoyl-*p*-nitrodiphenylamine yields *p*-azoxybenzoyldiphenylamine when the solution is not allowed to become too strongly alkaline; the substance forms yellow leaflets and melts at 178°. Further reduction gives the corresponding azo-compound, melting at 172°.

p-Nitrodiphenylamine gives *p*-aminodiphenylamine in yield of 70 per cent.

o- and *p*-Nitroanilines yield 70 per cent. and 86 per cent. respectively of the theoretical quantity of *o*- and *p*-phenylenediamine.

1-Nitro-2-ethoxynaphthalene yields 1-amino-2-ethoxynaphthalene. If, however, the reduction is carried out in a solution of ammonium acetate instead of sodium acetate, a comparatively small quantity of an azoxy-compound is obtained as intermediate product. T. E.

Ethyl β -Aminocrotonate. By ROBERT BEHREND, FERDINAND C. MEYER, and YNGVE BUCHHOLZ (*Annalen*, 1900, 314, 200–230. Compare Behrend and Dietrich, *Abstr.*, 1900, i, 120).—Although it has been supposed that the formula $\text{NMe}\begin{smallmatrix} \text{CO}\cdot\text{CH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}\text{CMe}$ expresses the constitution of α -dimethyluracil as well as of the β -modification (*loc cit.*), it is now found that the structure of the former substance is represented by the expression $\text{NH}\begin{smallmatrix} \text{CO}-\text{CH} \\ \text{CO}\cdot\text{NMe} \end{smallmatrix}\text{CMe}$. In the course of this investigation, the existence of two ethyl β -aminocrotonates was revealed (Behrend, *Abstr.*, 1899, i, 331, and Knoevenagel, *ibid.*, 478). The labile ester melts at 20°, and separates from light petroleum in large, prismatic crystals belonging to the monoclinic system [$a:b:c=0.97:1.1;\beta=53.5^\circ$]. The stable form, melting at 33°, crystallises in the same system [$a:b:c=1.0111:1.1:2.108;\beta=88^\circ 27' 14''$].

Ethyl iminoacetylmalonoanilate, $\text{NH}\cdot\text{CMe}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{NHPh}$, obtained in association with ethyl phenyluraminocrotonate when

phenylcarbimide acts on ethyl β -aminocrotonate, crystallises from alcohol in needles, and melts at $125-126^\circ$; the crystals belong to the monoclinic system [$a:b:c=1.627:1:1.045$; $\beta=78^\circ 0'$]. Alcoholic potassium hydroxide resolves the substance into aniline, ammonia, carbon dioxide, acetic acid, and acetylacetanilide; concentrated hydrochloric acid gives rise to aniline, ammonia, and carbon dioxide, whilst concentrated sulphuric acid converts it into ethyl acetylmalononanilate.

Ethyl phenyluraminocrotonate, $\text{NPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$, crystallises from light petroleum in broad needles, and melts at $98-99^\circ$; concentrated hydrochloric acid resolves it into carbon dioxide, aniline, and ammonia.

Phenylmethyluracil, $\text{NPh} \cdot \begin{smallmatrix} \text{CO} \cdot \text{CH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \rangle \text{CMe}$, prepared by heating ethyl phenyluraminocrotonate with alkali hydroxides, melts at $244-245^\circ$, and crystallises from hot water in microscopic, six-sided leaflets belonging to the monoclinic system [$a:b:c=1.41:1:1$]. *Dibromohydroxyphenylmethyluracil*, $\text{NPh} \cdot \begin{smallmatrix} \text{CO} \cdot \text{CBr}_2 \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \rangle \text{CMe} \cdot \text{OH}$, obtained by the action of bromine on finely divided phenylmethyluracil suspended in water, is an amorphous substance containing $1\frac{1}{2}\text{H}_2\text{O}$, and decomposes at 190° . *Bromophenylmethyluracil*, $\text{NPh} \cdot \begin{smallmatrix} \text{CO} \cdot \text{CBr} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \rangle \text{CMe}$, produced when dibromohydroxyphenylmethyluracil is heated with alcohol in a reflux apparatus, crystallises in nacreous leaflets, and melts at $241-242^\circ$, when it becomes brown.

Ethyliminoacetylmalonothionanilate, $\text{NH} \cdot \text{CMe} \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CS} \cdot \text{NPh}$, prepared from ethyl β -aminocrotonate and phenylthiocarbimide, melts at $135-136^\circ$, and crystallises from dilute alcohol in yellow prisms belonging to the monoclinic system [$a:b:c=1.463:1:1.040$; $\beta=76^\circ 34'$].

Thionphenylmethyluracil, $\text{NPh} \cdot \begin{smallmatrix} \text{CO} \cdot \text{CH} \\ \text{CS} \cdot \text{NH} \end{smallmatrix} \rangle \text{CMe}$, melts at $253-255^\circ$, and crystallises from hot dilute alcohol in colourless, six-sided leaflets belonging to the monoclinic system [$a:b:c=1.45:1:1$]. When heated with concentrated hydrochloric acid at 170° during 5 hours, it yields hydrogen sulphide and phenylmethyluracil. M. O. F.

Maleanilide. By WILLEM A. VAN DORP and P. M. VAN HAARST (*Rec. Trav. Chim.*, 1900, 19, 311-317).—When malephenylamic acid, $\text{CO}_2\text{H} \cdot \text{CH} \cdot \text{CH} \cdot \text{CO} \cdot \text{NPh}$, is heated at 100° with phosphorus oxychloride, a compound, $\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}_2\text{Cl}_2\text{P}$, is produced, which crystallises in yellow needles, decomposes when heated at 145° , and is decomposed by water with the formation of hydrochloric and phosphoric acids and of nearly the theoretical quantity of *maleanilide*, $\text{C}_2\text{H}_2(\text{CO} \cdot \text{NPh})_2$. Maleanilide crystallises in prisms melting at $175-180^\circ$, and is insoluble in water, but more or less soluble in organic solvents. The *hydrochloride*, $\text{C}_{16}\text{H}_4\text{O}_2\text{N}_2 \cdot \text{HCl}$, crystallises in yellow needles which decompose when heated to about 160° ; it is also decomposed by cold water, and when boiled with methyl alcohol is converted into maleanil, $\begin{smallmatrix} \text{CH} \cdot \text{CO} \\ \text{CH} \cdot \text{CO} \end{smallmatrix} \rangle \text{NPh}$, with elimination of aniline

hydrochloride. When fused, maleanilide is converted into the isomeric fumaranilide, which crystallises in needles melting at 312°.

From the mother liquors obtained in the preparation of the yellow compound, $C_{16}H_{15}O_4N_2Cl_2P$, chlorosuccinanyl, $\begin{matrix} CHCl \cdot CO \\ CH_2 - CO \end{matrix} > NPh$, was isolated; it crystallises in colourless needles melting at 118—119°.

N. L.

Action of Nitrosoacylamines on Primary Bases. By H. APITZSCH (*Ber.*, 1900, **33**, 3521—3525. Compare Abstr., 1899, i, 268).—When nitrosobenzoylbenzylamine (Abstr., 1899, i, 134) (1 mol.) and aniline (2 mols.) are heated together, first very gently and finally on the water-bath, until the evolution of nitrogen ceases, the products are benzanilide, benzylaniline, a little benzoic acid, and oily neutral substances. With *p*-toluidine, the products are *p*-benzotoluidide melting at 156—158°, and *benzyl-p*-toluidine, which was isolated in the form of *benzyltolylbenzenesulphonamide*, $CH_2Ph \cdot N(C_6H_4Me) \cdot SO_2Ph$; this crystallises in long, colourless needles melting at 123—124°.

Nitrosobenzoylbenzylamine and phenylhydrazine yield *s*-benzoylphenylhydrazine (Fischer, Abstr., 1878, 308), and probably benzylphenylhydrazine, but this could not be isolated.

J. J. S.

Two Dinitromethyl-*p*-toluidines. By JOHANNES PINNOW [and in part RICHARD MAYER] (*J. pr. Chem.*, 1900, [ii], **62**, 505—522. Compare Abstr., 1897, i, 338).—When β -dinitromethyl-*p*-toluidine is reduced with ammonium sulphide, it is converted into 5-nitromethyltolylene-2:4-diamine, $[Me:NH_2:NHMe:NO_2 = 1:2:4:5]$, which crystallises in long, lustrous brown leaflets, melts at 168°, and dissolves easily in acetone, ethyl acetate, glacial acetic acid, hot alcohol, chloroform, or hot benzene. The acetyl derivative crystallises in yellowish-brown prisms or needles, melts at 205·5—207°, and is soluble in most organic solvents, but only sparingly so in cold benzene, ether, or hot water. By the action of amyl nitrite on a solution of nitromethyltolylene-2:4-diamine in pyridine, dinitrodiaminodimethyldiazoaminotoluene is obtained in small, yellow prisms of the composition $3C_{16}H_{19}O_4N_7 \cdot 2C_5H_5N$; this substance melts and decomposes at 267·5°, is fairly soluble in hot pyridine or nitrobenzene, and, when heated, loses its pyridine of crystallisation; if reduced with zinc dust in neutral solution, it is converted into methyl-2:4:5-triaminotoluene.

When β -dinitromethyl-*p*-toluidine is reduced with zinc and hydrochloric acid, a mixture of γ -diamino-*p*-toluidine and diaminomethylcresol is produced; these substances may be separated by means of their acetyl derivatives. Triacetylmethyl-2:4:5-triaminotoluene crystallises in rhombic prisms, melts and decomposes at 257—258°, and is fairly soluble in hot water or hot alcohol. Diacetylmethyldiaminocresol crystallises in slender needles containing $1H_2O$, which it loses slowly at 115—125°; it melts at 151—152°, and dissolves easily in hot alcohol.

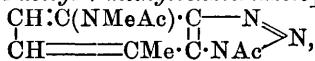
Diacetylmethyltolylene-2:4-diamine, obtained by the action of acetic

anhydride on methyl-*p*-tolylenediamine, crystallises in prisms, melts at 183—184°, and dissolves readily in the usual organic solvents when hot, but less readily in the cold; when heated with hydrochloric acid, trimethylbenzimidazole is produced.

Acetyl-β-dinitromethyltoluidine, prepared by the addition of sulphuric acid to a hot solution of 2:3-dinitromethyl-*p*-toluidine in acetic anhydride, crystallises from alcohol or pyridine in bright yellow needles, melts at 151°, and dissolves readily in acetone, chloroform, glacial acetic acid, benzene, hot alcohol, or ethyl acetate.

Nitromethyltolylenediamine, obtained by the reduction of 2:3-dinitromethyl-*p*-toluidine with alcoholic ammonium sulphide, crystallises in lustrous, nearly black prisms, melts at 127—128°, and is very easily soluble in chloroform, methyl alcohol, or hot benzene.

Methyl-2:3:4-triaminotoluene hydrochloride, obtained by reducing 2:3-dinitromethyl-*p*-toluidine with zinc and hydrochloric acid, crystallises in double truncated pyramids, and melts and decomposes at 161—171°; by the action of acetic anhydride, it is converted into *diacetylmethyl-2:3:4-triaminotoluene*, which crystallises in needles or prisms, melts at 198—198·5°, and is soluble in alcohol, chloroform, glacial acetic acid, acetone, ethyl acetate, benzene, or water. When *diacetylmethyl-2:3:4-triaminotoluene* is heated with glacial acetic acid, *4-acetyl-amino-1:2:5-trimethylbenzimidazole* is produced, which crystallises in needles, melts at 217—218°, and dissolves easily in alcohol or glacial acetic acid. By the action of nitrous acid on *diacetylmethyltriaminotoluene*, *diacetylmethylaziminotoluene* [*4-acetylmethylamino-1-acetyl-7-methylbenzotriazole*],



is obtained in slender, white needles; it melts at 169°, and is fairly soluble in alcohol and sparingly so in benzene, ether, or water.

Benzoyl-γ-dinitromethyltoluidine crystallises from alcohol in prisms and melts at 110·5°.

Acetyl-γ-dinitromethyltoluidine crystallises in slender, yellow needles, melts at 90·5°, and is soluble in most organic solvents; when reduced with zinc and hydrochloric acid, a substance is produced which crystallises in rhombic prisms, melts and decomposes at 222·5°, and appears to consist of a mixture of $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_3, x\text{H}_2\text{O}$ and $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_3\text{Cl}, x\text{H}_2\text{O}$.
E. G.

p- and *o*-Toluidinoacetic Acid and *α-p* and *α-o*-Toluidinopropionic Acid. By FRIEDRICH STEPPES (*J. pr. Chem.*, 1900, [ii], 62, 481—504).—The principal product of the action of monochloroacetic acid on *p*-toluidine is not *p*-toluidinoacetic acid (*p*-tolylglycine), as stated by Meyer (Abstr., 1896, i, 401) and by Schwebel (Abstr., 1878, 302), but a substance which melts at 174°, and is the *p*-toluidine salt of an acid; this acid, however, could not be isolated, on account of its instability. A small quantity of *p*-toluidinoacetic acid is produced; it melts at 120—121°, and is identical with the acid obtained by Meyer (*loc. cit.*) by the hydrolysis of its ethyl ester, and also with that prepared by Sieber (Abstr., 1899, i, 128) from the corresponding nitrile.

When monochloroacetic acid reacts with *o*-toluidine, a nearly quantitative yield of *o*-toluidinoacetic acid is obtained, as previously shown by Staats (Abstr., 1880, 387). If *o*-toluidine is treated with hydrocyanic acid, and the mixture added to a solution of formaldehyde (40 per cent.), *o*-toluidinoacetonitrile is obtained as a thick, uncrystallisable oil; it is converted by concentrated sulphuric acid into *o*-toluidinoacetamide, which crystallises in needles, melts at 140°, is easily soluble in hot water or alcohol, fairly so in warm benzene, and sparingly in ether, and on hydrolysis yields *o*-toluidinoacetic acid.

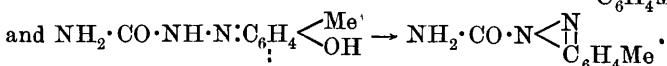
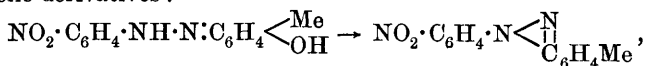
By the action of α -bromopropionic acid on *p*-toluidine, α -*p*-toluidinopropionic acid is produced almost quantitatively; it crystallises in pearly leaflets, melts at 158°, and is identical with the acid obtained by Tiemann and Stephan (Abstr., 1883, 199) from the corresponding nitrile.

α -*o*-Toluidinopropionic acid may be prepared by the action of α -bromopropionic acid on *o*-toluidine; it crystallises in colourless needles, melts at 118°, and dissolves readily in glacial acetic acid, alcohol, ether, or hot water. When an ethereal solution of *o*-toluidine and hydrocyanic acid is added to acetaldehyde, small, colourless needles, melting at 80–81°, and plates or prisms, melting at 96°, are produced in approximately equal quantities; the former are soluble in 20 per cent. hydrochloric acid, whilst the latter are insoluble. Both these substances yield α -*o*-toluidinopropionamide when dissolved in strong sulphuric acid; if the acid solution of the plates is poured into water, acetaldehyde is produced, but this does not occur in the case of the needles. The needles consist of α -*o*-toluidinoacetonitrile, whilst the plates have the composition: C, 74.73; H, 6.90; N, 19.33 per cent. The amide corresponds in its characters with that described by Tiemann and Stephan (*loc. cit.*), and on hydrolysis yields α -*o*-toluidinopropionic acid. E. G.

Mechanism of the Conversion of Arylhydroxylamines into Aminophenols. By EUGEN BAMBERGER (*Ber.*, 1900, 33, 3600–3622).—By the action of sulphuric acid, or of alum-solution, or occasionally by the action of water alone, on arylhydroxylamines, a *p*-aminophenol is usually produced, but when the para-position is occupied by a halogen, *o*-aminophenols are produced, and these occasionally appear even when the para-position is occupied by hydrogen; *p*-aminophenolsulphonic acids are occasionally formed, and ethyl- or methyl-alcoholic sulphuric acid gives rise to derivatives of *p*- or *o*-phenetidine or anisidine; other occasional products are *p*-aminodiphenylamine bases, *p*-hydroxydiphenylamines, quinols (the hydroxy-groups sometimes causing a methyl group to wander from the para- to the meta-position), resorcinol ethers, and polymeric benzylenimines.

These facts are explained by the assumption that water is first split off, $C_6H_5 \cdot NH \cdot OH \rightarrow C_6H_5 \cdot N<$, and that the product, if methylated in the para-position, may then pass into a benzylenimine, $Me \cdot C_6H_4 \cdot N< \rightarrow CH_2 : C_6H_4 \cdot NH$, but usually recombines with water to an 'iminoquinol' [imino- ψ quinol], $NH : C_6H_4 < \begin{smallmatrix} H \\ OH \end{smallmatrix}$; this usually passes directly into a *p*-aminophenol, $NH_2 \cdot C_6H_4 \cdot OH$, but may be

etherified to $\text{NH}\cdot\text{C}_6\text{H}_4\text{<}^{\text{H}}_{\text{OR}}$, or hydrolysed to $\text{O}\cdot\text{C}_6\text{H}_4\text{<}^{\text{H}}_{\text{OH}}$, or converted into a sulphate, $\text{NH}\cdot\text{C}_6\text{H}_4\text{<}^{\text{H}}_{\text{O}\cdot\text{SO}_3\text{H}}$, and thus give rise, by further isomeric change, to anisidines, phenetidines, quinols, and sulphonic acids. In the case of the para-methylated hydroxylamines, a number of the intermediate products can be isolated, although this has not been found possible in other cases, owing to the rapidity with which the changes occur. The 'iminoquinols' [imino- ψ -quinols] cannot be isolated, although they can be shown to be present, as they rapidly hydrolyse to the 'quinol' [ψ -quinol], $\text{O}\cdot\text{C}_6\text{H}_4\text{<}^{\text{CH}_3}_{\text{OH}}$, the constitution of which is proved by reduction to the phenol $\text{HO}\cdot\text{C}_6\text{H}_4\text{Me}$, and isomeric change to the bivalent phenol, $\text{HO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$; in presence of alcoholic sulphuric acid, the reversion to the true benzene structure takes place in two directions, by the wandering of the methyl group, $\text{O}\cdot\text{C}_6\text{H}_4\text{<}^{\text{CH}_3}_{\text{OH}} \rightarrow \text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OEt} [= 1:3:4]$, or by the wandering of the hydroxyl group, $\text{O}\cdot\text{C}_6\text{H}_4\text{<}^{\text{CH}_3}_{\text{OH}} \rightarrow \text{OEt}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OEt} [= 1:4:3]$. By the action of *p*-nitrophenylhydrazine or of semicarbazide, the 'quinols' [ψ -quinols] are converted into hydrazones or semicarbazones, which cannot be isolated, as they immediately lose water and give dieyclic derivatives:



The 'quinols' [ψ -quinols] are analogous to the alkali-insoluble oxidation products of the phenols and phenol-bromides (Auwers, Abstr., 1900, i, 161).
T. M. L.

Mesitylhydroxylamine and Nitrosomesitylene. By EUGEN BAMBERGER and ADOLF RISING (*Ber.*, 1901, 33, 3623—3636).—Mesitylhydroxylamine, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{NH}\cdot\text{OH}$, melts at 116° , and when quite pure can be kept in closed vessels for 3 weeks without decomposition, but usually changes into a mixture of nitrosomesitylene and mesidine, together with nitromesitylene and azomesitylene, which are probably formed from the preceding compounds; a similar decomposition is brought about by air-free solutions of sodium hydroxide, whilst water and dilute sulphuric acid give, in addition, a small amount of trimethyl- ψ -quinol, $\text{O}\cdot\text{C}_6\text{H}_2\text{Me}_3\cdot\text{OH}$ (see the following abstracts).

Phenylmesitylhydroxycarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_2\text{Me}_3$, prepared by the action of phenylcarbimide on mesitylhydroxylamine, crystallises from benzene in white, felted needles, and melts and decomposes at 116° .

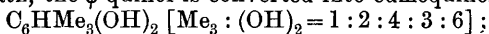
isoBenzaldoxime mesityl ether, $\text{C}_6\text{H}_5\cdot\text{CH}<^{\text{N}}_{\text{O}}\cdot\text{C}_6\text{H}_2\text{Me}_3$, prepared by the action of mesitylhydroxylamine on benzaldehyde, crystallises from light petroleum in transparent needles, melts at $101.5\text{--}102^\circ$, and is
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hydrolysed by dilute mineral acids. *p*-Nitroisobenzaldoxime mesityl ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_2\text{Me}_3 \\ \text{O} \end{smallmatrix}$, forms yellow needles, and melts at 156.5 — 157° . *m*-Nitroisobenzaldoxime mesityl ether forms yellowish-white needles and melts at 140.5 — 141° . *iso*Anisaldoxime mesityl ether $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_2\text{Me}_3 \\ \text{O} \end{smallmatrix}$, forms white, silky needles and melts at 152 — 152.5° .

Nitrosomesitylene, $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{NO}$, crystallises in glistening, iridescent, orthorhombic tablets or needles and melts at 122° to a green liquid; at the freezing point of benzene, the solutions consist chiefly of double molecules, and are almost colourless, whilst at the boiling point the solutions are green, and the molecular weight is normal; the substance is decomposed by boiling water into nitromesitylene and mesidine, together with a small quantity of trimethyl- ψ -quinol; unlike nitrosobenzene, it does not reduce Fehling's solution, and does not condense with the hydroxylamine to form an azoxy-derivative.

T. M. L.

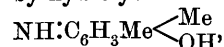
Mesityl- ψ -quinol. By EUGEN BAMBERGER and ADOLF RISING (*Ber.*, 1901, 33, 3636—3642).—*Mesityl- ψ -quinol*, $\text{O} \cdot \text{C}_6\text{H}_2\text{Me}_3 \cdot \text{OH}$ (compare preceding page), prepared by passing a current of air through mesityl-hydroxylamine suspended in water, crystallises from light petroleum in flat, white, glistening needles, and melts at 45.5 — 46° . The benzoyl derivative, $\text{O} \cdot \text{C}_6\text{H}_2\text{Me}_3 \cdot \text{OBz}$, forms glistening prisms and melts at 128.5° . By heating with sodium hydroxide in a current of hydrogen on a water-bath, the ψ -quinol is converted into cumoquinol,



it is also readily reduced by zinc and ammonium chloride, sulphurous acid, or ferrous sulphate and sodium hydroxide to mesitol, $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{OH}$.

T. M. L.

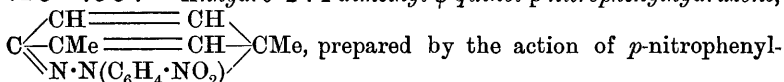
2:4-Dimethylphenylhydroxylamine and 2:4-Dimethyl- ψ -quinol. By EUGEN BAMBERGER and F. BRADY (*Ber.*, 1901, 33, 3642—3658).—*as-Azoxy-m-xylene*, $\text{N}_2\text{O}(\text{C}_6\text{H}_3\text{Me}_2)_2$, $[\text{Me}_2 : \text{N}_2\text{O} = 1 : 3 : 4]$, prepared by atmospheric oxidation of the hydroxylamine, forms glistening, yellow needles and melts at 76 — 76.5° . Dilute sulphuric acid at 100° converts the hydroxylamine into *as.m*-xylidine, nitroso-*m*-xylene, and azoxy-*m*-xylene, together with 2:4-dimethyl- ψ -quinol, and amino-*m*-xylene, $[\text{Me}_2 : \text{OH} : \text{NH}_2 = 1 : 4 : 2 : 5]$, which are probably produced by hydrolysis and reduction respectively from dimethylimino- ψ -quinol,



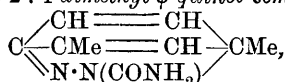
and 2:4-dimethylquinol, formed by isomeric change from the ψ -quinol, which is the chief product of the action. Similar products are obtained at atmospheric temperatures, or by the action of alum solution, but the proportion of dimethyl- ψ -quinol is larger.

2:4-Dimethyl- ψ -quinol hydrate, $\text{O} \cdot \text{C}_6\text{H}_3\text{Me}_2 \cdot \text{OH} + \text{H}_2\text{O}$, crystallises in glistening, colourless, rhombic prisms, melts at 53 — 54° (corr.), and loses its water on exposure to the air. The ψ -quinol forms glistening, colourless prisms, melts at 73 — 73.5° (corr.), dissolves moderately in

boiling water and readily in most organic solvents, and volatilises at 100° . Sodium hydroxide at 100° converts it into the isomeric 2:4-dimethylquinol, no trace of 4:6-dimethylresorcinol being produced; acids act similarly, but give a much smaller yield of the quinol; the ψ -quinol is also decomposed by light; it is very readily reduced to *as.m*-xenol. *Benzoyl-2:4-dimethyl- ψ -quinol*, $\text{O}:\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OBz}$, crystallises from light petroleum in clear, glistening prisms and melts at $72.5-73.5^{\circ}$. *Anhydro-2:4-dimethyl- ψ -quinol-*p* nitrophenylhydrazone*,



hydrazine on the quinol, crystallises from alcohol in glistening, dark orange-red needles, melts at $126.5-127^{\circ}$, and is insoluble in alkali hydroxides. *Anhydro-2:4-dimethyl- ψ quinol semicarbazone*,



separates in orange-red, silky flakes, and melts and decomposes at $134-135^{\circ}$. *2:4-Dimethylimino- ψ -quinol*, $\text{NH}:\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OH}$, has not been isolated in a pure state, but its presence is proved by continued decomposition into ammonia and the ψ -quinol. T. M. L.

Substance formed in the Iodination of Phenols. By WILHELM VAUBEL (*Chem. Zeit.*, 1900, 24, 1059—1060; 1077—1078).—When a solution of phenol in saturated aqueous sodium hydrogen carbonate is treated at 25° with an excess of a solution of iodine in aqueous potassium iodide, an insoluble red substance is formed. This contains 64.7—64.8 per cent. of iodine, corresponding with $1\frac{1}{3}$ I per mol. of phenol; when treated with alcoholic potash, it is converted into a white substance with 64.5 per cent. of iodine, and when reduced with zinc dust in alkaline alcoholic solution it forms a compound, $\text{C}_{18}\text{H}_{18}\text{O}_3$, which is a yellowish-brown powder soluble in alkalis, melts at $74-76^{\circ}$, and yields a bromo-derivative, $\text{C}_{18}\text{H}_{17}\text{O}_3\text{Br}$, when it is dissolved in acetic acid, and treated with aqueous potassium bromide, hydrochloric acid, and bromate.

Other phenols behave in a more or less similar manner when iodinated in sodium hydrogen carbonate solution, several molecules frequently condensing. The phenols are enumerated below, with the number of iodine atoms present in the product per mol. of the phenol. Salicylic acid, $1\frac{1}{3}$ (with elimination of the carboxyl group); *m*-cresol, 2—3; *o*-cresol dibromide, 1; *o*-nitrophenol, 1.6; *p*-nitrophenol, 3; tyrosine, 0.5. Similar results by other observers are quoted in addition.

C. F. B.

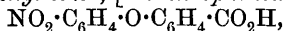
Aryl Hydrogen Sulphates. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1901, [iii], 25, 46—49).—A general method for the preparation of potassium aryl sulphates consists in adding the phenol to a cooled mixture of pyridine and chlorosulphonic acid in carbon disulphide solution, removing the carbon disulphide by distillation, and decomposing the double sulphate of pyridine and the phenol thus produced by distillation with potassium hydroxide solution. *Potassium eugenyl sulphate* is thus obtained in the form of white, nacreous scales

melting at 203°. When heated in acid solution it is decomposed, with the formation of eugenol and potassium hydrogen sulphate, whilst when boiled with excess of potash it is converted into potassium isoeugenyl sulphate which melts at 223°. This salt is readily converted into potassium vanillin sulphate by the action of oxidising agents, ozone being the most suitable. Potassium vanillin sulphate forms small, yellow crystals which decompose at 200°, and yields vanillin when heated with dilute sulphuric acid.

The method described has also been applied to the preparation of sodium phenyl sulphate, potassium phenyl sulphate, potassium thymyl sulphate melting at 80°, potassium β -naphthyl sulphate melting at 210°, potassium benzyl sulphate, which crystallises in brilliant, white needles melting at 233°, and potassium geranyl sulphate which does not crystallise. N. L.

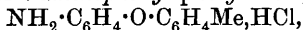
Derivatives of Phenyl Ether. By A. N. COOK and HOMER W. HILLYER (*Amer. Chem. J.*, 1900, 24, 525—529).—*o*-Nitrophenyl *p*-tolyl ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_4\text{Me}$, obtained by the action of *o*-bromonitrobenzene on the potassium derivative of *p*-cresol, crystallises in large, sulphur-yellow, monoclinic prisms, melts at 49°, boils at 220° under 25 mm. pressure, but suffers partial decomposition when distilled under the ordinary pressure; it is not volatile with steam; it dissolves easily in ether, acetic acid, chloroform, benzene, or hot alcohol.

2-Nitro-4'-carboxyphenyl ether, [4-*o*-nitrophenoxybenzoic acid],



prepared by oxidising *o*-nitrophenyl *p*-tolyl ether with a solution of chromium trioxide in glacial acetic acid, melts at 182—183°, crystallises from hot water in yellow needles, and is very soluble in glacial acetic acid or warm alcohol; its cadmium, silver, and barium salts are described.

The hydrochloride of *o*-aminophenyl-*p*-tolyl ether,



obtained by reducing the nitro-compound with tin and hydrochloric acid, crystallises in needles, and melts at 220°; the base may be precipitated from a solution of the hydrochloride, but rapidly decomposes; the platinumchloride melts and decomposes at 150°. E. G.

Derivatives of Cacodylic Acid. By A. ASTRUC and H. MURCO (*J. Pharm.*, 1900, [vi], 12, 553—556).—Guaiacol cacodylate (Barbary and Rebec, *Bull. Soc. Pharm.*, 1900, 11, 121) crystallises in small prisms which are soluble in alcohol, glycerol, or water; it is a very unstable salt, and on solution in water is immediately decomposed into cacodylic acid and guaiacol, which separates out in oily drops.

Cinnamylcacodylic acid, $\text{C}_8\text{H}_7 \cdot \text{CO}_2\text{H} \cdot \text{AsMe}_2\text{O} \cdot \text{OH}$, prepared by the direct combination of mol. proportions of cacodylic acid and cinnamic acid, crystallises in prisms melting at 79—81°, and is only slightly soluble in ether, glycerol, or oils, but dissolves readily in alcohol. Cinnamic acid is precipitated on the addition of water to its alcoholic solutions. When treated with water it is decomposed into cacodylic acid, which dissolves in the water, and cinnamic acid, which remains undissolved. H. R. LE S.

Polymeric Phenylisocrotonic Acid. By RUDOLPH FITTIG (*Ber.*, 1900, 33, 3519—3521).—When phenylisocrotonic acid is boiled for 6 hours with dilute hydrochloric acid (1 vol. commercial acid to 3 vols. of water), 65 per cent. of it is converted into phenylbutyrolactone; the reaction is never complete and the lactone when similarly boiled is partially converted into phenylisocrotonic acid. When stronger acid is employed, the polymeric phenylisocrotonic acid previously described (*Abstr.*, 1888, 595) is also formed. It has the molecular formula, $C_{22}H_{20}O_4$, and is a monobasic lactonic acid and not dibasic; when oxidised, it yields benzoic acid and thus the group C_6H_5 must be intact. An intermediate product on oxidation is the *ketonic acid*, $C_{20}H_{20}O_5$, melting at 132° ; when this is reduced, it is converted back into the lactonic acid; according to the author, this must contain the group, $CHPh \begin{smallmatrix} \ddot{C} \cdot \ddot{C} \\ \diagup \quad \diagdown \\ O \cdot CO \end{smallmatrix}$.

J. J. S.

***p*-Methyl-*o*-benzylbenzoic Acid.** By HEINRICH LIMPRICHT (*Annalen*, 1900, 314, 237—251. Compare *Abstr.*, 1898, i, 322).—*p*-Methyl-*o*-benzylbenzoic acid, $C_6H_4Me \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, crystallises from alcohol in large, six-sided plates, and melts at 133° ; the *sodium* salt crystallises in long needles containing $2H_2O$, and melts at 270° , the *silver* salt is anhydrous, and the *methyl* ester crystallises from alcohol in thin, lustrous leaflets, and melts at 126° . The *chloride* is a yellow oil which does not combine with hydrocarbons under the influence of aluminium chloride, and when heated changes very readily into methylanthranol.

β -Methylanthranol, $C_6H_4 \begin{smallmatrix} C(OH) \\ \diagup \quad \diagdown \\ CH \end{smallmatrix} > C_6H_3Me$, prepared by the action of concentrated sulphuric acid on *p*-methyl-*o*-benzylbenzoic acid, is also produced when the acid chloride is heated at 95° in a vacuum; it crystallises from alcohol in plates, melts at 100° , and sublimes in needles and leaflets when strongly heated. Chromic acid oxidises the substance to β methylanthraquinone. Solutions of methylanthranol in alkalis and alkali carbonates decompose rapidly, and besides methylanthraquinone, it has been found possible to isolate two *compounds* melting at 150° and 207° respectively; the latter has the composition $C_{30}H_{22}O_2$.

Nitrotolylphthalide, $C_6H_4 \begin{smallmatrix} C \\ \diagup \quad \diagdown \\ CO \cdot O \end{smallmatrix} > CH \cdot C_6H_3Me \cdot NO_2$, produced when methylbenzylbenzoic acid is dissolved in concentrated nitric acid, separates from alcohol in colourless crystals and melts at 137° . *Trinitro-methylbenzylbenzoic acid*, $C_{15}H_{11}O_8N_3$, forms small, white crystals, and melts at 213° ; the *barium* salt crystallises from water in colourless prisms. *Trinitrotoluoylbenzoic acid*, $C_{15}H_9O_9N_3$, crystallises from acetic acid in small prisms and melts at 215° ; the *barium* salt contains $3H_2O$.

Aminomethylbenzylbenzoic acid, $NH_2 \cdot C_6H_3Me \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, prepared by reducing nitrotolylphthalide and nitrotoluoylbenzoic acid with zinc dust and ammonia, crystallises from dilute alcohol in slender, white needles and melts at 155° ; the *barium* and *silver* salts are

anhydrous, and the *hydrochloride* and *nitrate* melt at 215° and 214° respectively.

M. O. F.

Dichlorohydroxybenzoic Acids. By N. TARUGI (*Gazzetta*, 1900, 30, 487—492).—The action of chlorine on potassium salicylate yields a mixture of mono- and di-chlorosalicylic acids. In presence of increasing quantities of potassium hydroxide, the proportion of dichloro-acid formed increases, until the mixture consists of 3 mols. of potassium hydroxide to 1 mol. of salicylic acid, when the disubstituted acid alone is formed together with a small quantity of chlorophenol. If the proportion of potassium hydroxide be further increased, the dichloro-acid diminishes in quantity and finally vanishes, the amount of 2 : 4-dichlorophenol formed showing a corresponding increase. The dichlorosalicylic acid formed in the above reaction has the constitution $[\text{CO}_2\text{H} : \text{OH} : \text{Cl}_2 = 1 : 2 : 3 : 5]$; when heated with lime, it yields 2 : 4-dichlorophenol, whilst with nitric acid the dichloronitrophenol $[\text{OH} : \text{Cl}_2 : \text{NO}_2 = 1 : 2 : 4 : 6]$ is obtained. Similarly, the action of excess of chlorine on a solution of 1 mol. of *p*-hydroxybenzoic acid in 3 mols. of potassium hydroxide solution yields the dichlorohydroxybenzoic acid of the constitution $[\text{CO}_2\text{H} : \text{Cl} : \text{OH} : \text{Cl} = 1 : 3 : 4 : 5]$; this acid with nitric acid gives 2 : 6-dichloro-4-nitrophenol, whilst when heated with lime it yields 2 : 6-dichlorophenol, which is also obtained in increasing quantities as the proportion of potassium hydroxide in the above reaction is increased beyond 3 mols. The action of chlorine on *o*-nitrophenol (1 mol.) dissolved in potassium hydroxide (3 mols.) solution yields 2 : 4-dichloro-6-nitrophenol, whilst when *p*-nitrophenol is employed, 2 : 6-dichloro-4-nitrophenol is obtained.

Thus when an excess of chlorine acts in alkaline solution on a disubstituted benzene derivative having an acid function, two atoms of chlorine enter the benzene nucleus and, in the case of *o*- or *p*-compounds, always take up given stable positions.

T. H. P.

Tautomerism of *o*-Benzoylbenzoic Acid. By ALBIN HALLER and ALFRED GUYOT (*Bull. Soc. Chim.*, 1901, [iii], 25, 49—56).—The unsuccessful attempts to prepare two methyl esters corresponding with the two hypothetical tautomeric forms of benzoylbenzoic acid have already been described (*Abstr.*, 1900, i, 170). It is now also shown that the acid behaves normally when heated with phenylcarbimide at 80°, diphenylcarbamide and benzoylbenzoic anhydride being formed. At the ordinary temperature, however, an unstable additive product seems to be produced.

N. L.

Tolylphthalide. By HEINRICH LIMPRICHT (*Annalen*, 1900, 314, 251—258).—Tolylphthalide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO}\cdot\text{O} \end{smallmatrix} > \text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$, crystallises in long,

flat, colourless needles melting at 129°, and distils under 15 mm. pressure without decomposing; it dissolves in alkalis and alkali carbonates, but the acid, of which salts are thereby produced, cannot be isolated. Ammonia and zinc dust convert it into methylbenzylbenzoic acid, and potassium permanganate oxidises it to toluoylbenzoic and benzophenonedicarboxylic acids.

Concentrated nitric acid converts the substance into nitrotolyl-

phthalide (this vol., i, 145) which melts at 137°. *Aminotolylphthalide*, $\text{C}_6\text{H}_4 > \text{CH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$, obtained by reducing the nitro-derivative with stannous chloride, crystallises in colourless, four-sided, rhombic plates melting at 144°; the *nitrate* and *hydrochloride* crystallise in slender, long needles, and the latter decomposes at 205°. *Trinitrotolylphthalide*, $\text{C}_{15}\text{H}_9\text{O}_8\text{N}_3$, crystallises from acetone in white, microscopic leaflets, and melts at 215°. M. O. F.

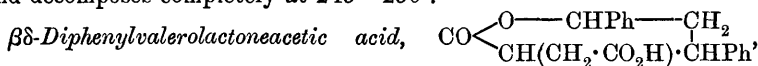
Isomeric Ammonia Derivatives of Ethyl Benzylidenebisacetoacetate. (Benzylideneacetoacetic- β -aminocrotonate or Phenylaminohepteneonedicarboxylate.) By PAUL RABE (*Ber.*, 1900, 33, 3803—3806).—Ethyl β -benzylidenebisacetoacetate is readily converted by ammonia into *ethyl δ -phenyl- β -amino- β -heptene- ζ -one- γ : ϵ -dicarboxylate*, $\text{NH}_2 \cdot \text{CMe} \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{CHPh} \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$, which exists in two distinct forms. The α -form consists of woolly needles, which melt at 58° and then pass into the β -form. The β -form separates from alcoholic solution in coarse, well-developed crystals melting at 98°. When water is added to an alcoholic solution of either form, a *hydrate* is produced which contains $1\text{H}_2\text{O}$, melts at about 72°, and over sulphuric acid loses water and yields the α -form. The two forms are alike in their behaviour towards alcoholic ferric chloride, and the exact nature of their isomerism has not yet been ascertained.

A. H.

Addition of Diethyl Succinate to $\alpha\beta$ -Unsaturated Ketones and Esters. By HANS STOBBE (*Annalen*, 1900, 314, 111—146. Compare Abstr., 1899, i, 900; 1900, i, 179).—[With KARL RUSSWURM].— *γ -Phenacyl- γ -phenylpyrotartaric acid*,



produced in the form of its sodium derivative when an ethereal solution of benzylideneacetophenone and diethyl succinate is added to sodium ethoxide suspended in ice-cold ether, crystallises from water or ether in rhombic plates, and melts at 175—177°; it is sparingly soluble in cold water, and requires 500 parts of hot benzene for dissolution. The *sodium* salt forms long needles containing $4\frac{1}{2}\text{H}_2\text{O}$, the *barium* salt contains $3\text{H}_2\text{O}$, and the *calcium* and *silver* salts are amorphous. The *dimethyl* ester crystallises from a mixture of ether and light petroleum in large plates melting at 77—79°, and the *diethyl* ester melts at 60—62°; the *anhydride* crystallises from a mixture of benzene and light petroleum in stellate aggregates of needles, and melts at 119—121.5°. The *oxime* is sparingly soluble in water, from which it separates in minute crystals, melting at 180—184°, when it becomes deep red; the *semicarbazone* melts and evolves gas at 194—198°, and forms a crystalline *sodium* derivative, which becomes yellow at 200°, and decomposes completely at 245—250°.



prepared by reducing γ -phenacyl- γ -phenylpyrotartaric acid with sodium amalgam, crystallises from 50 per cent. alcohol in lustrous needles, which soften at 170°, and melt between 185° and 187°. The *barium* salt of the

hydroxydicarboxylic acid, $C_{19}H_{20}O_3$, obtained by heating the lactone-acid with barium hydroxide, crystallises in leaflets.

When phenacylphenylpyrotartaric acid is oxidised with nitric acid, it is decomposed completely, yielding only benzoic acid and its products of nitration. Potassium permanganate, however, gives rise to β -benzoylpropionic and benzoylformic acids.

The compound, $C_{29}H_{26}O_4$, a bye-product in the preparation of γ -phenacyl- γ -phenylpyrotartaric acid, crystallises from 90 per cent. alcohol in slender needles, and melts at $224-227^\circ$.

[With RICHARD FISCHER].—*Methyl 2-benzoyl-3-phenylcyclopentanone-4-carboxylate*, $CO \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}(\text{COPh}) \quad \text{CH}(\text{CO}_2\text{Me}) \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{CHPh} \end{array}$, prepared by adding an ethereal solution of dimethyl- γ -phenacyl- γ -phenylpyrotartrate to sodium methoxide suspended in ether, and acidifying the product, crystallises from absolute alcohol in slender needles and melts at $115-116^\circ$; the *semicarbazone* melts and decomposes at $231-232^\circ$. M. O. F.

Dibenzoylmaleic and Dibenzoylfumaric Esters. By CARL PAAL and HEINRICH SCHULZE (*Ber.*, 1900, 33, 3784—3795).—Ethyl dibenzoylthylenedicarboxylate exists in *cis*- and *trans*-forms, the configurations of which have been determined by their reaction with hydrazine hydrate. This substance reacts with the *cis*-form almost quantitatively to produce a pyridazine derivative, whilst with the *trans*-form it only reacts slowly and incompletely to produce the same compound.

Ethyl dibenzoylmaleate (ethyl *cis*-dibenzoylthylenedicarboxylate), $CO_2Et \cdot \begin{array}{c} \text{C} \cdot \text{Bz} \\ | \\ \text{C} \cdot \text{Bz} \end{array}$, which was formerly described by Paal and Härtel (*Abstr.*, 1897, i, 598) as ethyl dibenzoylfumarate, when treated with hydrazine hydrate, readily yields *ethyl 3:6-diphenylpyridazine-4:5-dicarboxylate*, $N : CPh \cdot \begin{array}{c} \text{C} : CO_2Et \\ | \\ N : CPh \cdot \text{C} \cdot CO_2Et \end{array}$, which crystallises in long, flat, colourless needles melting at $127-128^\circ$. *Diphenylpyridazinedicarboxylic acid* crystallises in long needles containing 2 mols. of alcohol, and melts and decomposes at 202° . The *potassium* salt crystallises in silky needles, and the *silver* salt in sparingly soluble, microscopic needles. When the acid is heated above its melting point, it yields carbon dioxide and *3:6-diphenylpyridazine*, $CPh \begin{array}{c} \text{N} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{CH} : \text{CH} \end{array} CPh$, which crystallises in large, nacreous plates melting at $221-222^\circ$. The crystalline *hydrochloride*, *aurichloride*, and *platinichloride* are all decomposed by water.

Ethyl dibenzoylfumarate (ethyl *trans*-dibenzoylthylenedicarboxylate), $Bz \cdot \begin{array}{c} \text{C} \cdot CO_2Et \\ | \\ CO_2Et \cdot \text{C} \cdot Bz \end{array}$, is formed when the *cis*-compound is heated with a small amount of aniline in a closed vessel at 100° , and crystallises in well developed, colourless, asymmetric prisms melting at $87-88^\circ$. Both ethyl dibenzoylmaleate and ethyl dibenzoylfumarate are reduced by phenylmethylhydrazine to ethyl dibenzoylsuccinate. When the fumaric ester is treated with alcoholic potash at the ordinary temperature, pure potassium dibenzoylfumarate is formed, which crystallises

in flat needles containing alcohol. The *silver* salt, which is a faintly yellow, microcrystalline powder, is converted by ethyl iodide almost quantitatively into the original ethyl dibenzoylfumarate. When a solution of the potassium salt is acidified, the acid obtained is not dibenzoylfumaric acid, but dibenzoylmalic acid, $\text{CO}_2\text{H}\cdot\text{CBz}(\text{OH})\cdot\text{CHBz}\cdot\text{CO}_2\text{H}$ (Paal and Härtel). On the other hand, this acid does not yield corresponding salts, but when treated with the requisite amount of aqueous potash yields potassium dibenzoylfumarate. That the acid is not dibenzoylfumaric acid containing $1\text{H}_2\text{O}$ is proved by the fact that by heating the water cannot be removed without decomposition occurring (compare this vol., i, 154).

Ethyl dibenzoylmaleate is converted by hydrolysis into a mixture of potassium dibenzoylmaleate with a small amount of potassium dibenzoylfumarate. This mixture of potassium salts is decomposed by acids in a similar manner to potassium dibenzoylfumarate, dibenzoylmalic acid being produced.

A. H.

Lichens and their Characteristic Constituents. V. By OSWALD HESSE (*J. pr. Chem.*, 1900, [ii], 62, 430—480. Compare Abstr., 1898, i, 531, 679; 1899, i, 381; this vol., i, 85).—*Usnea plicata* from Java cinchona bark contains *d*-usnic acid, usnaric acid, usnarin and plicatic acid. Usnaric acid contains no alkyloxy-groups; when heated with alcoholic potassium hydroxide or aqueous barium hydroxide, it loses carbon dioxide, and a brown, amorphous substance is produced. If a solution of usnaric acid in acetic anhydride is heated for 24 hours and allowed to cool, a *substance*, which melts at 209° and is slightly soluble in alcohol, separates in white needles; on diluting the mother-liquor with water, another substance is obtained, which melts at 128° , and dissolves readily in alcohol; both these compounds exhibit an acid reaction, and do not give any coloration with ferric chloride. *Plicatic acid*, $\text{C}_{20}\text{H}_{38}\text{O}_8\cdot\text{OMe}$, is dibasic; it crystallises in lustrous, white leaflets, melts at 133° , dissolves easily in alcohol, acetone, or ether, and gives no coloration with ferric chloride; its *barium* salt was prepared.

Usnea barbata var. *dasydypoga* and *florida* yield *d*-usnic acid, usnaric acid and alecortic acid (see later).

Alectoria jubata var. *implexa* (*Bryopogon jubatum* var. *implexum*) contains not only salazinic acid as stated by Zopf (Abstr., 1898, i, 90), but also alecortic acid. *Alecortic acid* is dibasic; it dissolves sparingly in alcohol, ether, or hot glacial acetic acid, and crystallises from the last-mentioned solvent in needles; it melts and decomposes at 186° , gives a reddish-brown coloration with ferric chloride, contains no alkyloxy-groups, and is converted by acetic anhydride into a colourless resin; its *barium* and *potassium* salts are described. When this acid is heated with solution of barium hydroxide, the solution becomes dark red, and yields an *acid*, which crystallises in white needles, is more soluble in ether or alcohol than alecortic acid, and melts and decomposes at about 220° .

Evernia divaricata does not contain usnic acid as asserted by Zopf (Abstr., 1898, i, 90), but only divaricatic acid.

Ramalina cuspidata yields *cuspidatic acid*, $\text{C}_{16}\text{H}_{20}\text{O}_{10}$, which

crystallises in white needles, melts at 218° , dissolves easily in ether, acetone, or alcohol, and gives a violet-blue coloration with ferric chloride.

Thamnolic acid, $C_{19}H_{15}O_{10} \cdot OMe$, obtained from *Thamnolia vermicularis* (Abstr., 1899, i, 381), melts and decomposes at 213° ; when this acid is heated with barium hydroxide solution, it loses carbon dioxide and yields *thamnolinic acid*, $C_{16}H_{20}O_7$, which crystallises in long, colourless needles, melts at 163° , dissolves readily in alcohol, ether, glacial acetic acid, or hot water, and gives a purple coloration with ferric chloride.

Stereocaulon coralloides contains atranorin, a small quantity of usnetic acid, and an acid, which Zopf (Abstr., 1896, i, 103) seems to have mistaken for psoromic acid (parellic acid); this new acid crystallises in small, white needles, is soluble in hot glacial acetic acid, hot alcohol, hot acetone, or benzene, and gives a violet-blue coloration with ferric chloride; when heated, it does not melt, but darkens at 250° and is quite black at 260° .

The 'stereocaulic acid' obtained by Zopf from *S. alpinum* is identical with usnetic acid.

S. salazinum contains not only salazinic acid, as stated by Zopf (Abstr., 1897, i, 362), but also a considerable quantity of atranorin. Salazinic acid contains no alkyloxy-groups; it crystallises from hot alcohol in spherical, crystalline aggregates, and blackens at 260 — 262° without melting. It dissolves in dilute potassium hydroxide to form a yellow solution which rapidly darkens, and yields red crystals of the potassium salt of an acid, which is a decomposition product of salazinic acid; the same acid is produced when salazinic acid is dissolved in concentrated sulphuric acid.

Cladonia Floerkeana yields coccillic acid, as previously shown by the author (Abstr., 1899, 382), and also a small proportion of thamnolic acid. When coccillic acid is heated with hydriodic acid, it is converted into a mixture of rhizonic and coccillic acids, the former of which suffers decomposition with formation of methyl iodide, carbon dioxide, and betorcinol, whilst the latter remains unchanged. *Coccillic acid*, $C_{10}H_{12}O_4$, crystallises in white needles, melts at 176 — 177° , dissolves easily in ether or alcohol, and gives an intense violet-blue coloration with ferric chloride; if heated above its melting point, it decomposes and yields a crystalline sublimate, which is probably mesorcinol.

C. fimbriata (*e-chordalis*) yields protocetraric acid.

C. uncinata does not contain usnic acid, as stated by Knop (*Annalen*, 1844, 49, 124), but *uncinatic acid*, $C_{23}H_{28}O_9$, is obtained as a white, crystalline powder which melts and decomposes at 212° , is sparingly soluble in ether, chloroform, glacial acetic acid, or cold alcohol, but freely in hot alcohol, and gives a purple coloration with ferric chloride; its potassium, ammonium, and barium salts were prepared.

C. squamosa (*a-ventricosa*) yields *squamatic acid*, which crystallises in short prisms, melts and decomposes at 215° , has a slightly bitter taste, dissolves sparingly in ether, alcohol, benzene, chloroform, or acetone, and more easily in glacial acetic acid, and gives a purple coloration with ferric chloride; it contains one methoxyl group.

Parmelia tiliacea (*Imbricaria tiliacea*).—Re-examination of this

lichen has confirmed the opinion previously expressed by the author (Abstr., 1899, i, 382) that Zopf's 'parmelialic acid' is identical with lecanoric acid.

P. sorediata contains lecanoric acid but no atranorin.

P. perlata.—The lichen previously examined by the author consisted of a mixture of *P. perlata*, *P. perforata*, and *P. olivetorum*.

P. perlata yields atranorin and a trace of lecanoric acid.

P. perforata furnished atranorin and a small proportion of lecanoric acid, whereas Zopf (Abstr., 1898, i, 90) found salazinic acid and very little atranorin.

P. olivetorum proved on re-examination to contain atranorin and lecanoric acid, as previously stated (Abstr., 1898, i, 679), but not erythric acid, as Zopf asserts.

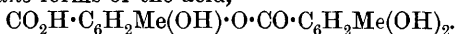
P. tinctorum (= *P. coralloides*) yields atranorin and 23.58 per cent. of lecanoric acid.

P. saxatilis var. *sulcata* furnished protocetraric acid only, whereas Zopf (Abstr., 1897, i, 436) found atranorin and 'stereocaulic acid.'

P. saxatilis var. *panniformis* contains atranorin, protocetraric acid, and usnetic acid (Abstr., 1877, ii, 896). Usnetic acid has the composition $C_{24}H_{26}O_8$, and not $C_9H_{10}O_3$ as previously stated; it melts at 192° . When usnetic acid is heated with barium hydroxide, it yields carbon dioxide and *usnetol*, $C_{23}H_{28}O_7$, which crystallises in white needles, melts at 166° , and is very soluble in ether or alcohol; a small quantity of another substance is also produced, which crystallises in white needles, and is soluble in ether, but differs from usnetol in being insoluble in solution of potassium hydrogen carbonate.

P. acetabulum contains atranorin and salazinic acid, as previously shown by Zopf (Abstr., 1898, i, 489).

Umbilicaria pustulata yields gyrophoric acid, which melts at $200-202^\circ$, dissolves easily in alcohol or acetone, is optically inactive, and contains no alkyloxy-groups. The formula $C_{18}H_{20}O_7$ was previously assigned to this acid, but the author now finds that it is isomeric with lecanoric acid, $C_{16}H_{14}O_7$. When gyrophoric acid is heated with glacial acetic acid, it is converted into orsellic acid; if boiled with alcohol, it yields orsellic acid and ethyl orsellate; under other conditions, the acid decomposes into orcinol and carbon dioxide. The author considers that gyrophoric and lecanoric acids are probably the *cis*- and *trans*-forms of the acid,



Placodium saxicolum var. *compactum* furnishes atranorin, and a crystalline acid, which is soluble in alcohol or ether.

P. gypsaceum yields parellic acid, but no usnic acid, as stated by Zopf (Abstr., 1898, i, 90).

P. circinatum contains parellic acid.

Icmadophila ceruginosa furnished only an uncrystallisable brown oil, whereas Bachmann obtained icmadophilic acid.

Blastenia arenaria var. *teicholytum* (*Callopisma teicholytum*).—Re-examination of this lichen has confirmed the author's view (Abstr., 1899, i, 382) that it contains atranorin and gyrophoric acid.

Hæmatomma ventosum contains *d*-usnic acid, divaricatic acid, and an acid which does not possess the properties of the ventosaric acid de-

scribed by Zopf (Abstr., 1897, i, 364), but rather resembles alecortic acid.

Lecanora subfusca yields atranorin, as found by Zopf (Abstr., 1897, i, 436).

Aspicilia calcarea furnishes *aspicilin*, which crystallises in white prisms, melts at 178.5° , dissolves readily in hot alcohol, glacial acetic acid, chloroform, or benzene, but less easily in ether; when heated strongly, it sublimes and distils without decomposition. This lichen also contains oxalic acid and erythric acid (Abstr., 1898, i, 532), which the author now considers to be either erythrolecanoric or erythroglyphoric acid.

Urcularia scruposa var. *arenaria* yields a small proportion of lecanoric acid.

Lecidea grisella furnishes gyrophoric acid.

Graphis scripta yields salazinic acid.

An appendix to the paper contains a detailed criticism of Zopf's recent work (this vol., i, 87). E. G.

Usnic Acid. Rotation of other Lichen Acids. By HEINRICH SALKOWSKI (*Annalen*, 1900, 314, 97—111. Compare Widman, Abstr., 1900, i, 235).—The author has examined specimens of usnic acid derived from more than twenty different lichens, and finds that although considerable variations in the melting point occur, the limits of specific rotatory power are comparatively narrow.

Analyses of the insoluble yellow barium, strontium, and calcium salts of usnic acid are given.

Rhizocarpic acid is optically active, but atranoric, chrysophanic, pinastric, soloric, usnolic, and vulpic acids, and calicyn, are inactive.

M. O. F.

Action of β -Naphthol on Aldehydes. By M. ROGOFF (*Ber.*, 1901, 33, 3535—3538).—In continuation of Claisen's work (Abstr., 1887, 494) the author has prepared the following compounds by heating β -naphthol with aldehydes and acetic acid in closed tubes at 190 — 200° .

$C_{28}H_{20}O_3$, from vanillin, separates from glacial acetic acid in microscopic needles melting at 211° . $C_{28}H_{18}O_3$, from piperonaldehyde, crystallises in six-sided tablets melting at 237° . $C_{30}H_{24}O$, from cuminaldehyde, forms microscopic tablets and melts at 238° . $C_{28}H_{20}O_2$, from anisaldehyde, forms six-sided plates melting at 208° . $C_{27}H_{18}O_2$, from salicylaldehyde, crystallises in long prisms and melts at 208° .

These compounds are all of the type $CHR < \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} > O$, and are insoluble in alkalis; when warmed with sulphuric acid, they assume varying tints of red, and at the same time exhibit a greenish fluorescence. A. L.

Intramolecular Rearrangement of *iso*Aldoxime Ethers. By FRIEDRICH WEGENER (*Annalen*, 1900, 314, 231—236. Compare Neubauer, Abstr., 1898, i, 134).—Contrary to a previous conclusion,

the transformation of benzyl-*m*-nitrosobenzaldoxime into *m*-nitrobenzylisobenzaldoxime is reversible. The same remark applies to the relation between *o*-chlorobenzylisobenzaldoxime and benzyl-*o*-chloroisobenzaldoxime.

M. O. F.

Benzophenone-*o*-sulphonic Acid and some of its Homologues. By CARL KRANNICH (*Ber.*, 1900, **33**, 3485—3494).—Details are given for preparing ammonium *o*-sulphobenzoate from its imide ("saccharin"); it forms orthorhombic crystals [$a : b : c = 0.6686 : 1 : 1.2103$]. *o*-Sulphobenzoic acid crystallises with $3\text{H}_2\text{O}$ and melts at 69° , the anhydrous acid melting at 134° .

The following compounds were prepared by heating *o*-sulphobenzoic anhydride in presence of acetyl chloride with benzene and its homologues.

Benzophenonesulphonic [*benzoylbenzenesulphonic*] acid,
 $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$,

is very soluble in water, and cannot be obtained crystalline. The ammonium salt, with $1\text{H}_2\text{O}$, forms monoclinic crystals [$a : b : c = 1.9224 : 1 : 1.5921$; $\beta = 108^\circ 20'$] and melts at 202° ; the potassium salt (Remsen and Saunders, *Abstr.*, 1895, i, 474), with $1\text{H}_2\text{O}$, melts at 211° ; the sodium salt, with $4\text{H}_2\text{O}$, melts at 60° , the anhydrous salt melting at 236° ; the barium salt, with $1\text{H}_2\text{O}$, melts at 197 — 198° .

p-Methylbenzoylbenzene-*o*-sulphonic acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, prepared from toluene, is very deliquescent; the ammonium salt, with $1\text{H}_2\text{O}$, melts at 104° ; the potassium salt, with $1\text{H}_2\text{O}$, melts at 248° ; the sodium salt, with $4\text{H}_2\text{O}$, melts initially at 53° , and, when anhydrous, at 247° ; the barium salt, with $1\text{H}_2\text{O}$, melts at 215° . The structure of the acid follows from its yielding *p*-toluic acid when fused with alkali.

The substance obtained by the interaction of *m*-xylene and *o*-sulphobenzoic anhydride in presence of aluminium chloride is, by analogy with similar reactions (*Abstr.*, 1882, 848, and 1896, i, 462), probably 2 : 4-dimethylbenzoylbenzene-*o*-sulphonic acid, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$; it crystallises in slender, white needles with $2\text{H}_2\text{O}$, melts at 80° , and yields an ammonium salt, with $\frac{1}{2}\text{H}_2\text{O}$, melting at 235 — 236° . The potassium salt (anhydrous) melts and darkens at 300° ; the sodium salt could not be obtained crystalline; the barium salt, with $2\text{H}_2\text{O}$, melts at 207° .

The ψ -cumene derivative is probably a 2 : 4 : 5-trimethylbenzoylbenzene-*o*-sulphonic acid, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ (compare *Abstr.*, 1887, 940); it crystallises from chloroform in slender, white needles, sinters at 167° , melts at 169° , and yields an easily soluble, crystalline ammonium salt melting at 255 — 256° ; the potassium salt melts and decomposes at 286° ; the sodium salt, with $1\frac{1}{2}\text{H}_2\text{O}$, sinters at 272° and melts at 274° ; the barium salt melts at 267° .

s-Trimethylbenzoylbenzene-*o*-sulphonic acid, obtained by using mesitylene, crystallises from water, in which it is sparingly soluble, in colourless, lustrous plates, with $4\text{H}_2\text{O}$, which melt at 98° , lose their contained water at 100 — 110° , and then melt at 184° ; the ammonium salt melts at 272° , the potassium salt begins to sinter at 315° , the sodium salt, with $1\text{H}_2\text{O}$, melts at 171° , whilst the barium salt, with $4\text{H}_2\text{O}$, sinters at 248° and melts at 252° .

W. A. D.

Action of Nitrogen Tetroxide on the Benzilmonoximes. By GIACOMO PONZIO (*J. pr. Chem.*, 1900, [ii], 62, 543—544).—When an ethereal solution of α - or γ -benzilmonoxime is treated with nitrogen tetroxide, benzil, *p*-nitrobenzil, and small quantities of benzoic and *p*-nitrobenzoic acids are produced, but neither phenyldinitromethane nor its benzoyl derivative is formed. E. G.

The Stereoisomeric Symmetrical Dibenzoylethylenes. By CARL PAAL and HEINRICH SCHULZE (*Ber.*, 1900, 33, 3795—3800. (Compare this vol., i, 148).—When dibenzoylmalic acid is heated above its melting point, it loses water and carbon dioxide, and is converted into a mixture of the two stereoisomeric dibenzoylethylenes.

trans-Dibenzoylene, $\begin{array}{c} \text{Bz} \cdot \text{C} \cdot \text{H} \\ | \quad | \\ \text{H} \cdot \text{C} \cdot \text{Bz} \end{array}$, is the chief product of this decomposition, and crystallises in long, deep yellow needles melting at 111°. By reduction, it is converted into diphenacyl and combines with bromine to form *dibenzoylene bromide*, $\text{COPh} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{COPh}$, which crystallises in small, white prisms melting at 178°. When warmed with hydrazine hydrate, it yields about 25 per cent. of the calculated amount of 3:6-diphenylpyridazine. It also combines with aniline to form *anilinodibenzoylene* (anilinodiphenacyl), $\text{NHPh} \cdot \text{CHBz} \cdot \text{CH}_2\text{Bz}$, which crystallises in thin, sulphur-yellow prisms melting at 138° and is decomposed by boiling with acetic acid into the original *trans*-dibenzoylene and aniline.

cis-Dibenzoylene, $\begin{array}{c} \text{Bz} \cdot \text{C} \cdot \text{H} \\ | \quad | \\ \text{Bz} \cdot \text{C} \cdot \text{H} \end{array}$, which is only formed in small amount by the decomposition of dibenzoylmalic acid, crystallises in colourless, silky needles melting at 134°, and is more readily soluble in most reagents than the *trans*-modification. By hydrazine hydrate in the cold, it is converted quantitatively into 3:6-diphenylpyridazine and hence must have the *cis*-configuration. It unites with aniline to form the same anilinodiphenacyl as the *trans*-form, and also forms a *dibromide*. A. H.

Thermochemistry of Quinones: Constitution of Quinhydrones. By AMAND VALEUR (*Ann. Chim. Phys.*, 1900, [vii], 21, 470—574).—The thermochemical data relating to the unsubstituted quinones and their dihydro-derivatives have already been published (*Abstr.*, 1898, ii, 420, 500). The following constants have been determined for the chlorine derivatives of quinone (see table, p. 155).

The heats of oxidation of the monochloro-, dichloro-, trichloro-, and tetrachloro-quinols to the corresponding quinones are 29.4, 35.6, 46.7, and 45.3 Cal. respectively.

The substitution of two chlorine atoms by two hydroxyl groups in the formation of chloroanilic acid from chloroanil is accompanied by a generation of 92 Cal.; this value approximates to the heat change which attends the production of a dibasic acid from its dichloride, the heat of hydrolysis of malonic chloride being 103.7 Cal.

Sodium chloroanilate is described as a red compound crystallising with $4\text{H}_2\text{O}$; the author has obtained another hydrate containing $3\text{H}_2\text{O}$ which forms opaque, black crystals; the latter separates from concen-

| | Heat of combustion. | | Heat of formation from elements. | Heat of substitution of chlorine for hydrogen. |
|-----------------------------|---------------------|--------------------|----------------------------------|--|
| | Constant volume. | Constant pressure. | | |
| Chloroquinone | 618·5 Cal. | 618·2 Cal. | 56·0 Cal. | 32·6 Cal. |
| Chloroquinol | 647·6 | 647·6 | 95·6 | 30·6 |
| 2 : 6-Dichloroquinone | 580·9 | 580·4 | 64·2 | 62·8 |
| 2 : 6-Dichloroquinol | 615·9 | 615·7 | 97·9 | 54·6 |
| Trichloroquinone | 548·6 | 547·8 | 67·2 | 87·8 |
| Trichloroquinol | 595·0 | 594·5 | 89·5 | 68·2 |
| Tetrachloroquinone | 520·1 | 519·0 | 66·4 | 109·0 |
| Tetrachloroquinol | 566·1 | 564·3 | 90·1 | 90·8 |
| Chloroanilic acid | 487·3 | 486·2 | 158·4 | |

trated solutions at 35°, whilst the former is produced at 18°. The paper contains a detailed account of the estimation of halogens in organic compounds by the calorimetric bomb, and a description of a method for the quantitative estimation of quinones (compare Abstr., 1900, ii, 57 and 172). The action of hydroxylamine on the quinones under varying conditions has been studied; it is found to reduce the *p*-quinones with considerable generation of heat, and in this way, tetrachloroquinol is readily obtained from chloroanil.

The thermochemical data deduced from the study of the quinone-monoximes have already been published (Abstr., 1898, ii, 500).

A quinhydrone is produced by the direct combination of a quinone of higher molecular weight with the dihydro-derivative of a quinone of lower molecular weight, and the same product is obtained by mixing the less complex quinone with the quinol of higher molecular weight. In the second mode of formation, the first action is probably the oxidation of the quinol by the quinone of lower molecular weight, owing to the fact that the heat of reduction of the simpler quinone is greater than that of the quinone of higher molecular weight.

This hypothesis is justified by the fact that quinone and dihydroxyphenanthrene interact, forming quinol and phenanthraquinone.

The author discusses the formulæ suggested by Graebe and by Jackson and Oenslager for quinhydrones and suggests the following

constitution, $\text{CH} \begin{array}{c} \text{CH}_2-\text{CO} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \\ \diagdown \quad \diagup \\ \text{CO}-\text{CH}_2 \end{array} \text{CH}$, as being most in accordance with the properties of these compounds. G. T. M.

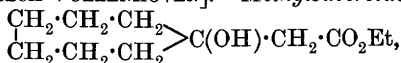
Terpenes and Ethereal Oils. By OTTO WALLACH (*Annalen*, 1900, 314, 147—167).—[With JULIUS SALKIND].—*Ethyl β-methylcyclo-*

hexanolacetic acid, $\text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2$
 $\text{CH}_2-\text{CH}_2-\text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ produced by the action of zinc on a mixture of methylhexanone and ethyl bromoacetate, is a liquid having the odour of ethyl benzoate; it boils at 127—129° and 254—256° under pressures of 21 mm. and 760 mm.

respectively, has a sp. gr. 1.0035, and n_D 1.4581 at 18°. The *methyl* ester boils at 120—125° and 240° under pressures of 23 mm. and 760 mm. respectively.

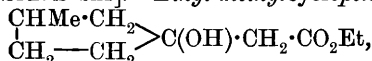
Ethyl β-methylcyclohexeneacetate, $C_7H_{11} \cdot CH_2 \cdot CO_2Et$, obtained on heating ethyl methylhexanolacetate with finely powdered potassium hydrogen sulphate at 160° during 2—3 hours, boils at 111—112° and 229—231° under pressures of 23 mm. and 760 mm. respectively, has a sp. gr. 0.9555, and n_D 1.46207 at 20°. The *methyl* ester boils at 103—105° and 214—217° under pressures of 23 mm. and 760 mm. respectively; it has a sp. gr. 0.97 and n_D 1.4635 at 25°. *β-Methylcyclohexeneacetic acid*, $C_7H_{11} \cdot CH_2 \cdot CO_2H$, boils at 146—149° and 245—255° under pressures of 23 mm. and 760 mm. respectively; it has a sp. gr. 1.015 and n_D 1.4807 at 27°. The *amide* crystallises from dilute methyl alcohol in colourless leaflets and melts at 149—150°.

[With VAN BEECK-VOLLENHOVEN].—*Methylsuberolacetate*,



prepared from suberone and methyl bromoacetate under the influence of zinc, boils at 141—145° and 249—257° under pressures of 12 mm. and 760 mm. respectively; it has a sp. gr. 1.037 and n_D 1.47017 at 20°. *Methyl subereneacetate*, $C_8H_{13} \cdot CO_2Me$, obtained from the foregoing substance and potassium hydrogen sulphate, boils at 125—126° under 13 mm. pressure; the *ethyl* ester boils at 135—136° under 23 mm. pressure. *Subereneacetic acid*, $C_9H_{14}O_2$, is a viscous liquid which boils at 158—159° under 17 mm. pressure, has a sp. gr. 1.035 and n_D 1.4920 at 20°. The *hydrocarbon*, C_8H_{14} , produced when subereneacetic acid is distilled under atmospheric pressure, boils at 138—140°, has a sp. gr. 0.824, and n_D 1.4611 at 20°; its constitution is probably represented by the expression $\begin{array}{c} CH_2 \cdot CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \cdot CH_2 \end{array} > C:CH_2$, the formula of a methylenecycloheptane.

[With NICOLAI SPERANSKI].—*Ethyl methylcyclopentanolacetate*,



produced by the influence of zinc on *β-methylcyclopentanone* and ethyl bromoacetate, boils at 115—120° under 12 mm. pressure; the *methyl* ester boils at 110—115° under 12 mm. pressure. The unsaturated *ester*, $C_6H_8Me \cdot CO_2Et$, prepared by the action of potassium hydrogen sulphate, boils at 88—91° under 15 mm. pressure.

2-Methyl-5-isopropylphenylacetic acid, $C_6H_3MePrs \cdot CH_2 \cdot CO_2H$, melts at 69—70°, and boils at 180—183° under 15 mm. pressure; cold fuming nitric acid converts it into the *dinitro-derivative*, $C_{12}H_{14}O_6N_2$, which crystallises from dilute methyl alcohol in white leaflets and melts at 196—197°. The *ethyl* ester, obtained from carvone and ethyl bromoacetate, boils at 155° under 15 mm. pressure.

Dihydrocarveolacetic acid, $OH \cdot C_{10}H_{16} \cdot CH_2 \cdot CO_2H$, boils at 196—208° under 14 mm. pressure, and when distilled under atmospheric pressure yields an unsaturated hydrocarbon, which should be homo-limonene; the *ethyl* ester, prepared from dihydrocarvone and ethyl bromoacetate, boils at 150—170° and 282—288° under pressures of

14 mm. and 760 mm. respectively, has a sp. gr. 0.997, and n_D 1.47664 at 20°.

[With LEIMBACH].—*Thujoleacetic acid*, $\text{OH} \cdot \text{C}_{10}\text{H}_{16} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallises from a mixture of benzene and petroleum in leaflets, and melts at 90—91°; the *ethyl ester*, prepared from thujone and ethyl bromoacetate, boils at 154—164° under 14 mm. pressure. *Isothujoleacetic acid* melts at 168—170°. M. O. F.

Condensation of Methylhexanone with Ethyl α -Bromopropionate and Ethyl α -Bromoisobutyrate. By JULIUS VON BRAUN (*Annalen*, 1900, 314, 168—177. Compare foregoing abstract).—*Ethyl methylcyclohexanolpropionate*, $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 - \text{CH}_2 - \text{C}(\text{OH}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}' \end{array}$ prepared by the action of zinc on methylcyclohexanone and ethyl α -bromopropionate, boils at 128—133° under 8 mm. pressure; hydrolysis does not yield the acid, but gives rise to a mixture of methylcyclohexanone, methylcyclohexanol, and propionic acid.

Ethyl methylcyclohexanolisobutyrate, $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 - \text{CH}_2 - \text{C}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}' \end{array}$ obtained from methylcyclohexanone and ethyl α -bromoisobutyrate, boils at 134—139° under 10 mm. pressure; sodium ethoxide resolves it into methylcyclohexanone and butyric acid. When the hydroxy-ester is heated with potassium hydrogen sulphate at 150—160°, the unsaturated ester, $\text{C}_{13}\text{H}_{22}\text{O}_2$, is produced, boiling at 116° under 8 mm. pressure; the acid from this compound, when heated under the ordinary pressure, yields the hydrocarbon, $\text{C}_{10}\text{H}_{18}$, which must be a menthene of the meta-series. M. O. F.

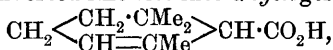
Compounds of the *cycloCitral Series*. By FERDINAND TIEMANN [and R. SCHMIDT] (*Ber.*, 1900, 33, 3703—3710).—The conversion of the open chain ketone, ψ -ionone, into the *cyclocitral* derivative, ionone, by the agency of acids (Tiemann and Krüger, *Abstr.*, 1894, i, 82) is now recognised as a change undergone by all compounds of the citral series. Further investigation of ionone has shown that this substance is a mixture of two isomerides, α - and β -ionones, which do not correspond with isomeric ψ -ionones.

In the following papers, to which the present communication is an introduction, the isomerism of the two modifications is proved to be dependent on the position of the unsaturated linking; it is also found that the production of two isomeric *cyclocitral*s characterises the action of acids on other members of the citral group. The constitution of *cyclocitral*s belonging to the α - and β -series is represented by the formulæ $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH} = \text{CMe} \end{array} \text{CHR}$ and $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 - \text{CMe} \end{array} \text{CR}$ respectively. M. O. F.

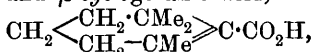
Inversion of Compounds belonging to the Citral Series. By FERDINAND TIEMANN [with R. SCHMIDT] (*Ber.*, 1900, 33, 3710—3713).—The inversion of geraniolene is effected in three days by continued agitation with 65 per cent. sulphuric acid. The *cyclogeraniolene* boils between 130° and 140°, the major portion distilling at 138° (uncorr.), and when oxidised with potassium permanganate yields isogeronic

acid, derived from the α -cyclogeraniolene, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH} = \text{CMe} \end{smallmatrix} \text{CH}_2$, and geronic acid from β -cyclogeraniolene, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 - \text{CMe} \end{smallmatrix} \text{CH}$.

Geranic acid is converted likewise into α -cyclogeranic acid,



which melts at 106° , and β -cyclogeranic acid,



which has not been yet obtained in crystals.

M. O. F.

Constitution of α -cycloGeranic Acid. By FERDINAND TIEMANN and HERMANN TIGGES (*Ber.*, 1900, 33, 3713—3719).—The *isogeranic* acid of Tiemann and Semmler (*Abstr.*, 1894, i, 85), which melts at 106° , will be called α -cyclogeranic acid, in order to distinguish it from the aliphatic *isogeranic* acid (Tiemann, *Abstr.*, 1900, i, 275) and from the β -cyclogeranic acid which corresponds with β -ionone. Experiments on the oxidation of this compound have shown that it has the constitution $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH} = \text{CMe} \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H}$.

Dihydroxydihydrocyclogeranic acid, $\begin{smallmatrix} \text{CH}_2 - \text{CMe}_2 - \text{CH} \cdot \text{CO}_2\text{H} \\ \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CMe} \cdot \text{OH} \end{smallmatrix}$, produced on oxidising α -cyclogeranic acid with potassium permanganate (Tiemann and Semmler, *loc. cit.*), melts at 198 — 200° ; the *ethyl* ester crystallises from petroleum, and melts at 92° . *Hydroxyketodihydrocyclogeranic acid*, $\begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ \text{CH}_2 - \text{CO} - \text{CMe} \cdot \text{OH} \end{smallmatrix}$, which is also formed, crystallises from water or from ethyl acetate and petroleum in prisms melting at 145° ; the semicarbazone melts at 216° .

isoGeranic (4-dimethylheptan-6-onic) acid (compare Tiemann and Schmidt, *Abstr.*, 1898, i, 377), produced when the dihydroxy- and ketohydroxy-acids are oxidised with chromic acid, yields the semicarbazone melting at 198° .

The *hydrogen ethyl* salt of α -acetyl- $\beta\beta$ -dimethyladipic acid, $\text{CO}_2\text{Et} \cdot \text{CHAc} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by oxidising ethyl dihydroxydihydrocyclogeranic acid with chromic acid, is an oil; the *semicarbazone* crystallises from absolute alcohol and melts at 157° . When this ester is heated with aqueous potassium hydroxide in a reflux apparatus, it undergoes the ketone hydrolysis, yielding *isogeranic* acid, $\text{CMe} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$.

M. O. F.

cycloCitral. By FERDINAND TIEMANN [with R. SCHMIDT] (*Ber.*, 1900, 33, 3719—3725).—Although compounds of the citral series, $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CHR}$, give rise to the *cyclocitral*s by union of the carbon atoms in positions 1 and 6, citral itself is converted into cymene. If, however, the sensitive aldehyde group is protected, as in citralidenecyanoacetic acid (Tiemann, *Abstr.*, 1900, i, 331), the normal cyclic product can be obtained.

β -cycloCitral, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 - \text{CMe} \end{smallmatrix} \text{C} \cdot \text{CHO}$, obtained by inverting

a and *b* citralidenecyanoacetic acids, and hydrolysing the *cyclo*-acids produced, is nearly colourless, has the odour of carvone, and boils at 88—91° and 95—100° under pressures of 10 mm. and 15 mm. respectively; it has sp. gr. 0.959 and 0.957 at 15° and 20° respectively, and n_D 1.49715 at 15°. The *semicarbazone* crystallises from methyl alcohol in large, transparent prisms containing the solvent, and melting at 165—166°; boiling ethyl acetate deposits it in thin leaflets melting at 166—167°. The additive *compound* of semicarbazide and *cyclocitral*, having the composition $C_{11}H_{21}O_2N_3$, instead of $C_{11}H_{19}ON_3$, crystallises from a mixture of ethyl acetate and benzene in slender needles, and decomposes at 250°. β -*cyclo*Citral yields β -ionone when condensed with acetone.

β -*cyclo*Geranic acid, $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot CMe_2 \\ \text{CH} - CMe \end{smallmatrix} > C \cdot CO_2H$, formed when the aldehyde is exposed to air, crystallises from petroleum in large, transparent prisms or plates, and melts at 93—94°; it decolorises bromine very slowly, yielding hydrogen bromide. Oxidation with alkaline permanganate gives rise to the *hydroxy-acid*, $C_{10}H_{16}O_3$, which melts and decomposes at 186°, and the *keto-acid*, $C_9H_{15}O_3$, which melts at 189°, and yields a *semicarbazone* melting at 240°; the main product of oxidation is *aa*-dimethylglutaric acid. M. O. F.

Constitution of α -Ionone. By FERDINAND TIEMANN [and R. SCHMIDT] (*Ber.*, 1900, 33, 3726—3727).—The constitutional formula, $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot CMe_2 \\ \text{CH} = CMe \end{smallmatrix} > CH : CH \cdot COMe$, for α -ionone is established by converting the ketone into *isogeronic acid* under the influence of ice-cold potassium permanganate followed by chromic acid. M. O. F.

Constituents of West Indian Sandalwood Oil. II. By HUGO VON SODEN and WILHELM ROJAHN (*Chem. Centr.*, 1900, ii, 1274—1275; from *Pharm. Zeit.*, 45, 878. Compare *Abstr.*, 1900, i, 401).—Attempts to separate amyrol into two components by fractionally distilling in a vacuum have shown that it probably consists of two secondary or tertiary sesquiterpene alcohols. Of these the *alcohol*, $C_{15}H_{25} \cdot OH$, of higher boiling point, present in the larger proportion, is a very viscous liquid, boils at 299°, has a sp. gr. of about 0.987 at 15°, and a rotation of about +36°. The second alcohol has not been isolated in a pure state, but appears to have the composition $C_{15}H_{23} \cdot OH$, and to be optically inactive.

From West Indian sandalwood oil, 0.1 per cent. of *amyrolin*, $C_{14}H_{12}O_3$, has also been isolated; it crystallises from methyl alcohol in stout crystals, is colourless, odourless, and tasteless, melts at 117°, and dissolves in hot alcohol or in alcoholic potash, giving in the former case a solution with a blue and in the latter a solution with a yellowish-green fluorescence. By the action of bromine in glacial acetic acid, a soluble and an insoluble product are formed. The latter is probably a *dibromide*, $C_{14}H_{12}Br_2O_3$; it is a white powder and melts at 157—159°. Amyrolin appears to be an aromatic compound of the character of a lactone. E. W. W.

Oil of Sweet Orange. By KARL STEPHAN (*J. pr. Chem.*, 1900, [ii], 62, 523—535).—The author has investigated the constituents of a large sample of the essential oil of sweet orange-peel which possessed the following characters: sp. gr. 0.851 at 15°; $[\alpha]_D + 96.3'$ at 20°; n_D 1.47245 at 20°; the residue left on evaporation amounted to 2.29 per cent.

After the removal of the terpenes by fractional distillation under 14 mm. pressure, the residual oil was shaken with sodium hydrogen sulphite solution; by this means, *n*-decaldehyde was separated, which boils at 93—94° under 12 mm. and at 207—209° under 755 mm. pressure, has a sp. gr. 0.828 at 15° and n_D 1.42977 at 15°. When *n*-decaldehyde is treated with β -naphthylamine and pyruvic acid, a substituted naphthacinchonic acid, $C_{23}H_{27}O_2N$, is obtained, which crystallises in white needles and melts at 237°. *n*-Decoic acid is produced when *n*-decaldehyde is oxidised with silver oxide; it has a sp. gr. 0.895 at 30° and 0.889 at 37°, and n_D 1.43078 at 30°. The author was unable to confirm the statements of Semmler (*Abstr.*, 1891, 539) and Parry (*Chemist and Druggist*, 1900, 462, 722) that the oil contains citral, or that of Flatau and Labbé (*Abstr.*, 1899, i, 422) that a small proportion of citronellal is present.

The oil remaining from the bisulphite treatment, when hydrolysed with alcoholic potassium hydroxide, yielded *n*-octoic acid. The alcohols were dried and treated with phthalic anhydride; an ester was produced which on hydrolysis furnished *n*-nonyl alcohol of sp. gr. 0.840 at 15° and n_D 1.43582 at 15°. The portion which was not converted into an ester was carefully fractionated under 22 mm. pressure; *d*-linalool (coriandrol) was found in the earlier fractions, whilst the later fractions consisted of *d*-terpineol which gave $[\alpha]_D + 95.9'$. *d*-Terpineol yields a nitrosochloride which is converted by piperidine into the terpenylnitropiperidine melting at 159°; it also combines with phenylcarbimide with formation of terpenylphenylurethane. The alcohol obtained by Wright (*Annalen*, 1884, 227, 289) and supposed to be myristicol is *d*-terpineol.

The residue is a waxy mass which melts at 67—68° and gives a saponification number 65; it yields on hydrolysis a solid, saturated acid, $C_{27}H_{54}O_2$, melting at 77—78°, and an oil which solidifies on cooling, and melts at 138°; the latter substance gives Liebermann's cholesterol reaction, and appears to be related to phytosterol. When the residue is left for several days with warm sulphuric acid (32 per cent.), a substance separates in yellow crystals which melts at 192—193°, and contains 6.9 per cent. of sulphur.

The quantitative composition of the oil is as follows: terpenes, 96 per cent.; compounds containing oxygen, 1 per cent.; residue, 3 per cent. The compounds containing oxygen consist of *n*-decaldehyde, 5.7 per cent.; ester ($C_{10}H_{17}O_2C_8H_{15}$), 8.5 per cent.; nonyl alcohol, 7.0 per cent.; *d*-terpineol, 39.4 per cent.; and *d*-linalool, 39.4 per cent.

E. G.

Ononin. By FRANZ VON HEMMELMAYR (*Ber.*, 1901, 33, 3538—3540. Compare Hlasiwetz, *J. pr. Chem.*, 1855, 65, 419).—Onospin has the formula $C_{28}H_{32}O_{12}$, and its melting point is 172°, not 162° as given by Hlasiwetz.

On subjecting onospin to acid hydrolysis in the mode recommended by Hlasiwetz, an impure product is obtained melting indefinitely at 140—150°. After several crystallisations from dilute alcohol and subsequent extraction with water, a compound is obtained in white, glistening needles melting at 122°, but in quantity too small for analysis. The portion undissolved by water, after repeated extraction, yields a mixture of two substances, one in the form of long, flat needles melting at 155—157°, the other in white leaflets melting at 158—160°. The former, on analysis, gave numbers almost identical with those found by Hlasiwetz for his ononetin, so that the crude material is probably a mixture of isomerides $(C_{11}H_{10}O_3)_n$. In accordance with the above formula for onospin, its hydrolysis may be represented by the equation $C_{28}H_{32}O_{12} = C_{22}H_{20}O_6 + C_6H_{12}O_6$. A. L.

Sugars of Xanthorhamnin and Quercitrin. By EMIL VOTOČEK and V. FRIČ (*Zeit. Zuckerind. Böhm.*, 1900, 25, 1—7).—Besides rhamnose, xanthorhamnin yields galactose on hydrolysis, the ratio between the quantities of the two sugars obtained being 2 mols. of anhydrous rhamnose to 1 mol. of galactose. Quercitrin yields no sugar but rhamnose on hydrolysis. T. H. P.

Conversion of Hyoscyamine into Atropine by means of Sodium Alkyl oxides in Alcoholic Solution. By ARRIGO MAZZUCHELLI (*Gazzetta*, 1900, 30, ii, 476—487).—The conversion of hyoscyamine into atropine by means of (1) a methyl alcohol solution of sodium methoxide, (2) sodium ethoxide in ethyl alcohol, (3) an alcoholic solution of sodium hydroxide, and (4) sodium propoxide in propyl alcohol, has been studied. The mean values of K for the various cases are (1) 0.001295, (2) 0.00788, (3) 0.00764, and (4) 0.0114. Solution (2), prepared by dissolving sodium in absolute alcohol, and solution (3), obtained by dissolving carefully dehydrated sodium hydroxide in absolute alcohol, show identical behaviour. The energy of the sodium alkyl oxides, as given by the velocity with which they convert hyoscyamine into atropine, does not appear to depend on the extent to which they are electrolytically dissociated, as the transformation proceeds most quickly in the solvent having the smallest ionising power. T. H. P.

Action of Ethyl Iodide on Caffeine. By A. I. ROSSOLIMO (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 727—732).—*Caffeine ethiodide*, $C_8H_{10}O_2N_4 \cdot EtI$, prepared by heating caffeine with excess of ethyl iodide in a sealed tube at 160—170° for 20 hours, separates from absolute alcohol in short, pale yellow, acicular crystals which melt with evolution of gas at 182—183°, have a bitter taste, and are readily soluble in water, which, however, quickly decomposes them.

Caffeine ethochloride, formed on heating an alcoholic solution of the iodide with an excess of freshly precipitated silver chloride, crystallises from alcohol in colourless, transparent, superposed plates or from a mixture of alcohol and benzene in thin, silky, white rods melting at 182—183°. Its *platinichloride* is precipitated as an orange powder composed of microscopic acicular crystals which readily decompose on heating. The *aurichloride* separates from alcohol in microscopic, lemon-yellow, acicular crystals melting at 188°. T. H. P.

Action of Bromine on Cinchonidine. Two Isomeric α - and β -Dibromocinchonidines. By J. GALIMARD (*Bull. Soc. Chim.*, 1901, [iii], 25, 84—88).—When cinchonidine sulphate is heated with fuming hydrobromic acid and the liquid subsequently neutralised with ammonia, or sodium carbonate, cinchonidine hydrobromide, $C_{19}H_{22}ON_2HBr$, is precipitated as a nearly white powder which is very soluble in hot alcohol, but insoluble in water or ether.

When cinchonidine sulphate is warmed with bromine in dilute hydrobromic acid solution and the liquid left to cool, α -dibromocinchonidine hydromide, $C_{19}H_{20}Br_2ON_2 \cdot 2HBr$, crystallises out in colourless needles, which melt and decompose at $205-206^\circ$. When treated with ammonia or sodium carbonate, it yields α -dibromocinchonidine, which decomposes without melting at 180° . One of the atoms of bromine in α -dibromocinchonidine has probably replaced the hydrogen of a hydroxyl group, since it is readily removed by boiling with water or alkalis, or by the action of silver nitrate.

α -Dibromocinchonidine is unstable, and on keeping, or when treated with nitric acid, it is converted into the isomeric β -dibromocinchonidine. α -Dibromocinchonidine hydrobromide also, when subjected to prolonged boiling with alcohol, yields more highly brominated compounds, including a mixed hydrobromide of dibromocinchonidine and tribromocinchonidine, $C_{19}H_{20}ON_2Br_2 \cdot C_{19}H_{19}ON_2Br_3 \cdot HBr$, which, on treatment with lime, is converted into β -dibromocinchonidine. This base forms colourless crystals decomposing at 200° without melting, and is laevorotatory; bromine is not removed from it by treatment with aqueous alkalis or by silver nitrate. N. L.

The Formula of Cotarnine. By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 3685—3686).—A reply to Decker (*Abstr.*, 1900, i, 683).

A. H.

2-Ethylpiperidine and its Properties. By ANDREAS LIPP (*Ber.*, 1900, 33, 3513—3519. Compare Ladenburg, *Abstr.*, 1898, i, 339).—The compound obtained by the reduction of picolylalkine (compare *Abstr.* 1897, i, 230) is shown to be 2-ethylpiperidine. A number of

| | 2-Ethylpiperidine. | | 1-Methyl-2-ethylpiperidine. | |
|---------------------|--|---|---|--|
| | Ladenburg. | Lipp. | Ladenburg. | Lipp. |
| Boiling point | 141—143° | $\left\{ \begin{array}{l} 142-143^\circ \\ \text{corr. at} \\ 719 \text{ mm.} \end{array} \right\}$ | 150—151.5° | $\left\{ \begin{array}{l} 153.5-154.5^\circ \\ \text{at 730 mm.} \end{array} \right\}$ |
| Sp. gr. at 0° | 0.8666 | 0.8651 | 0.8515 | 0.8541 |
| Hydrochloride.... | m. p. 178—181° | 181—182° | | 153—154° |
| Platinichloride ... | $\left\{ \begin{array}{l} \text{m. p. } 189^\circ \\ \text{decomposes} \\ \text{at } 191^\circ \end{array} \right\}$ | $\left\{ \begin{array}{l} \text{melts and} \\ \text{decomposes} \\ \text{at } 208-210^\circ \end{array} \right\}$ | $\left\{ \begin{array}{l} \text{not} \\ \text{obtained} \\ \text{crystalline} \end{array} \right\}$ | crystalline |
| Aurichloride | m. p. 129—130° | 129—130° | 122—123° | 118—119° |
| Mercuric chloride. | | | | 202—205° |

derivatives have been prepared and investigated, but the properties of these differ only slightly from those given by Ladenburg. J. J. S.

d- and *l*-2-Ethylpiperidine. By HANS FRESE (*Ber.*, 1900, 33, 3483—3484).—The author corrects the values for the physical constants of *d*- and *l*-2-ethylpiperidine formerly given by Ladenburg (*Annalen*, 1888, 247, 71). The pure *d*-tartrate melts at 105·5° and yields a base which distils at 142—143·5° and has a sp. gr. 0·8680 at 4°; $[\alpha]_D + 17·5^\circ$. The *l*-tartrate was not obtained pure; the derived base boils at 138—142° and has $[\alpha]_D - 14·55^\circ$. W. A. D.

The Occurrence of Intermediate Products in the Synthesis of Pyrroles from 1:4-Diketones. By LUDWIG KNORR and PAUL RABE (*Ber.*, 1900, 33, 3801—3803).—When ethyl β -diacetylsuccinate is treated with dry ammonia gas at 0° in the presence of ether, it dissolves and the solution then deposits ethyl β -amino- β -hexene- ϵ -one- γ -dicarboxylate, $\text{NH}_2 \cdot \text{CMe} \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$, in compact, well-developed crystals. This substance gradually loses the elements of water when it is preserved, and passes into ethyl 2:5-dimethylpyrrole-3:4-dicarboxylate, a change which also occurs when it is dissolved in acetic acid, hot alcohol, or dilute mineral acids. The aminohexenone compound evolves ammonia when treated with concentrated aqueous soda and reacts with hydrazine hydrate to form bis-3-methylpyrazolone. Ethyl diacetylsuccinate therefore forms an intermediate aminoketone when treated with ammonia, and in this respect resembles the $\alpha\gamma$ -ketones and some of the $\alpha\epsilon$ -ketones, such as ethyl benzylideneacetoacetate. A. H.

Compounds of Bismuth Salts with Organic Bases. By CLEMENTE MONTEMARTINI (*Gazzetta*, 1900, 30, ii, 493—494).—A preliminary note, published on account of the appearance of a paper by Hauser and Vanino (*Abstr.*, 1900, i, 641).

On adding pyridine to an ethereal solution of bismuth chloride, a white precipitate is obtained, consisting of a double salt of 1 mol. of bismuth chloride with 1·5 mols. of pyridine. T. H. P.

Constitution of Platinum Bases. By SOFUS M. JORGENSEN (*Zeit. anorg. Chem.*, 1900, 25, 353—377. *Abstr.*, 1900, i, 542).—Several methods are described for the preparation of platopyridinetriammine chloride, $\text{PtPy}(\text{NH}_3)_3\text{Cl}_2 \cdot \text{H}_2\text{O}$. The salt crystallises in lustrous, white, rhombic tablets; when heated at 120—130°, it loses ammonia and pyridine and yields a bright yellow powder containing the compounds $\text{Pt}(\text{NH}_3)_3\text{Cl}_2$, PtPyNH_3Cl , and PtPy_2Cl_2 ; heated with hydrochloric acid on the water-bath, it yields the compound $\text{PtPyNH}_3\text{Cl}_2$ and platosammine chloride; with potassium platinochloride, it yields the salt $\text{PtPyNH}_3\text{Cl}_2 \cdot \text{PtCl}_2 \cdot \text{H}_2\text{O}$, which is very characteristic, crystallises in flat, crimson needles, and is decomposed by heating at 115°.

Anderson's salt, PtPy_2Cl_4 , Balbiano's salt, and chloroplatinsemi-pyridine chloride, when reduced with sodium thiosulphate, all yield the platopyridineammine chloride α , whereas the chloroplatinpyridine chloride, PtPy_2Cl_4 , corresponding with Gerhardt's chloride, is not reduced by sodium thiosulphate, and when treated with hydrogen sulphide yields the platopyridineammine chloride β .

Ethylenediamine platinochloride, $\text{PtC}_2\text{H}_4(\text{NH}_2\text{Cl})_2$, when heated with water on the water-bath, is converted into platosemiediethylenediamine chloride.

These reactions are in harmony with the view that Peyrone's chloride is the symmetrical compound, $\text{Cl}\cdot\text{NH}_3\cdot\text{Pt}\cdot\text{NH}_3\cdot\text{Cl}$, and Reiset's chloride the unsymmetrical compound, $\text{Cl}\cdot\text{NH}_3\cdot\text{NH}_3\cdot\text{Pt}\cdot\text{Cl}$. E. C. R.

Compounds of Metallic Salts with Bases of the Pyridine Series. By DANIEL TOMBECK (*Ann. Chim. Phys.*, 1900, [vii], 21, 433—469. Compare this vol., i, 135).—The halogen salts of zinc and cadmium combine with two molecular proportions of the corresponding salts of the aromatic amines to form compounds of the type $\text{ZnCl}_2\cdot 2\text{NH}_3\text{PhCl}$; pyridine also forms an analogous derivative, $\text{ZnCl}_2\cdot 2\text{C}_5\text{H}_5\text{N}\cdot\text{Cl}$. Two mols. of a pyridine base unite with 1 mol. of a halogen salt of zinc or cadmium to form a salt of the type $\text{CdCl}_2\cdot 2\text{C}_6\text{H}_7\text{N}$, and the combination has been effected in the case of picoline, lutidine, and collidine. These bases also form similar compounds with silver bromide, iodide, and cyanide, but the chloride interacts only with picoline.

The connection between the dissociation pressures of these double compounds and the temperature has been studied; the results obtained are tabulated, and the paper also contains the corresponding dissociation pressure curves. G. T. M.

Action of Bromine on 3-Picoline. By E. DEHNEL (*Ber.*, 1900, 33, 3498—3500).—A *monobromo-derivative*, $\text{C}_5\text{NH}_4\cdot\text{CH}_2\text{Br}$, is the principal product when 3-picoline is heated with bromine (2 mols.) and concentrated hydrochloric acid for 10 hours at 150° ; the base was not isolated owing to its instability, but was converted into the *picrate*, which crystallises from benzene in rosettes of yellow needles, melts at 114° , and on boiling with water for 2 hours yields the *picrate* of 3-picolylalkine (3-hydroxymethylpyridine), $\text{C}_5\text{NH}_4\cdot\text{CH}_2\cdot\text{OH}$, in the form of long, yellow needles. The *base*, formed on decomposing this salt, could not be obtained pure, but the *aurichloride* forms small, yellow crystals melting at 136 — 137° , and the *platinichloride*, brownish-red plates melting at 193 — 195° .

More complex derivatives of 3-picoline were also formed in the bromination; on distilling in a vacuum, a liquid boiling at 40 — 50° , and a solid distilling at 90 — 100° , were isolated, both apparently having the composition $\text{C}_{12}\text{H}_{10}\text{N}_2\text{Br}_5$. W. A. D.

Hantzsch's Synthesis of Ethyl Dihydrocollidinedicarboxylate. By PAUL RABE and ADOLF BILLMANN (*Ber.*, 1900, 33, 3806—3811. Compare this vol., i, 147).—Both the mono- and diethyl esters of ethylidenebisacetoacetic acid are converted by alcoholic ammonia at 0° into *ethyl β -amino- δ -methyl- β -heptene- ζ -one- γ : ϵ -dicarboxylate*, $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CHMe}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, which forms large, well-developed, non-fluorescent triclinic crystals melting at 140° . It is not affected by alkalis, and by phenylhydrazine is converted into the *phenylhydrazone* of *ethyl ethylidenebisacetoacetate*,
 $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CHMe}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$,

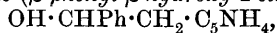
which crystallises in needles melting at about 203° . Ethyl dihydrocollidinedicarboxylate could not be obtained by the action of ammonia on ethyl ethylidenebisacetoacetate, and the statement of Knoevenagel and Klages (*Annalen*, 1894, 281, 105) must therefore be inaccurate. This fact also shows that in Hantzsch's synthesis of ethyl dihydrocollidinedicarboxylate from ethyl acetoacetate and aldehyde ammonia, ethyl ethylidenebisacetoacetate cannot be formed as an intermediate product.

Ethyl methylenebisacetoacetate, on the other hand, as stated by Knoevenagel, readily forms ethyl dihydrolutidinedicarboxylate.

A. H.

***o*-Nitrophenyl-2-picolyalkine and its Derivatives; Phenyl-2-picolyalkine.** By E. ROTH (*Ber.*, 1900, 33, 3476—3479).—*o*-Nitrophenyl-2-picolyalkine (β -*o*-nitrophenyl- β -hydroxy-2-ethylpyridine), $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_4$, obtained by heating 2-picoline with *o*-nitrobenzaldehyde and water for 7—8 hours at 137 — 140° , separates from dilute alcohol in snow-white crystals, melts at 137 — 138° , is not volatile with steam, and yields an *aurichloride* which forms prisms and melts at 155° ; the *platinichloride* melts at 212° , the green *ferrocyanide* at 148° with decomposition, and the *picrate* at 161° . The *acetate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OAc}) \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_4$, crystallises from alcohol and melts at 82° . *o*-Aminophenyl-2-picolyalkine (β -*o*-aminophenyl- β -hydroxy-2-ethylpyridine), obtained by reducing the nitro-compound with zinc or iron and hydrochloric acid, separates from alcohol as a snow-white mass which melts at 97 — 98° , and becomes red in the air; the *picrate*, *platinichloride*, and *ferrocyanide* were prepared.

Phenyl-2-picolyalkine (β -phenyl- β -hydroxy-2-ethylpyridine),



obtained by heating 2-picoline with benzaldehyde and water for 10 hours at 135° , crystallises from dilute alcohol in white leaflets and melts at 96 — 97° ; the *platinichloride*, with $3\text{H}_2\text{O}$, melts at 104° , the *aurichloride* at 131 — 132° , and the *mercurichloride* at 162° .

W. A. D.

2-Phenyl-6-stilbazole and 2-Phenyl-6-*o*-hydroxystilbazole. By E. DEHNEL (*Ber.*, 1900, 33, 3494—3497).—2-Phenyl-6-stilbazole (2-phenyl-6-styrylpyridine), $\text{C}_6\text{H}_5 \cdot \text{C}_5\text{NH}_3 \cdot \text{CH} \cdot \text{CHPh}$, obtained by heating 2-methyl-6-phenylpyridine (Scholtz, Abstr., 1895, i, 562) with benzaldehyde for 5—6 hours at 250 — 260° , crystallises from dilute alcohol in beautiful, white needles and melts at 79° ; the *hydrochloride*, with $4\text{H}_2\text{O}$, crystallises from dilute hydrochloric acid in long needles melting at 100° , and in yellow plates from alcohol or acetone. The *aurichloride* forms thick, red crystals and melts at 179° , and the *platinichloride* melts at 220° ; the *zincchloride* forms yellow crystals. With bromine, the base yields the compound $\text{C}_{19}\text{H}_{15}\text{NBr}_4 \cdot \text{HBr}$, which forms rose-coloured, six-sided plates, melts at 172° , and, when boiled with alcohol, yields 2-phenyl-6-stilbazole dibromide, $\text{C}_5\text{NH}_3 \cdot \text{Ph} \cdot \text{CHBr} \cdot \text{CHPhBr}$, in the form of lustrous, white leaflets melting at 190° ; on reduction, the base gives rise to 2-phenyl-6-stilbazoline, $\text{C}_5\text{NH}_3 \cdot \text{Ph} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Ph}$, which forms a non-crystallisable, white syrup, and yields a *hydrochloride* crystallising from water in stellar aggregates of white needles,

which darken at 160° and decompose at 200°; the *platinichloride* melts at 155—156°.

2-Phenyl-6 : o-hydroxystilbazole (2-phenyl-6 : o-hydroxystyrylpyridine), $C_5NH_3Ph \cdot CH : CH \cdot C_6H_4 \cdot OH$, obtained by heating salicylaldehyde with 2-phenyl-6-methylpyridine for 8—10 hours at 200°, crystallises from benzene in spherular aggregates of white needles and melts at 138°; the *hydrochloride* forms dark yellow needles and melts at 126—127°; the *aurichloride* brownish-red needles melting at 189°; the amorphous *platinichloride* melts at 190°. W. A. D.

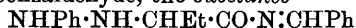
Sulphur Derivatives of Aromatic Amines. By ALBERT EDINGER (*Ber.*, 1900, 33, 3769—3770).—This is a preliminary paper, occasioned by Gutbier's communication (this vol., i, 96). From acridine and flowers of sulphur *mesothioacridone* is obtained; this has, presumably, the constitution $C_6H_4 \begin{smallmatrix} CS \\ \text{NH} \end{smallmatrix} C_6H_4$, and is analogous to Graebe's mesoacridone (*Abstr.*, 1893, i, 650), from which it can be obtained by the action of phosphorus and sulphur at 260°. It crystallises in red needles and melts at 275°; phosphorus pentachloride converts it into Graebe's mesochloroacridine, phosphorus and bromine into *mesobromoacridine*, which melts at 119°, and forms *mesoiodoacridine*, melting at 169°, when it is treated with alcoholic sodium iodide. It dissolves in alkalis, and from the solution *benzyl* and *benzoyl* derivatives, $C_{13}H_8N \cdot S \cdot CH_2Ph$ and $C_{13}H_8N \cdot SBz$, can be prepared.

C. F. B.

3 : 3'-Dichlorobenzidine. By PAUL COHN (*Ber.*, 1901, 33, 3551—3554).—3 : 3'-Dichlorobenzidine was made by reducing *o*-nitrochlorobenzene with zinc dust and sodium hydroxide and heating the resulting hydrazo-compound with strong hydrochloric acid; it is identical with the base prepared by chlorinating diacetylbenzidine (German Patents, 94410 and 97101). The *hydrochloride*, $C_{12}H_{10}N_2Cl_2 \cdot 2HCl$, dissolves readily in alcohol, but is sparingly soluble in water; the latter statement is also true of the *sulphate*, *nitrate*, and *oxalate*. The *platinichloride* is unstable. The *dibenzoyl* derivative, $C_{12}H_6Cl_2(NHBz)_2$, crystallises from xylene in bundles of white needles and melts at 265°.

3 : 3'-Dichlorobenzidine yields a *tetrazo*-dye on uniting the diazotised substance with naphthionic acid; this has a bluish-red tint and its colour, unlike that of the simple congo red, is not altered by dilute acetic acid; it is best used in faintly acid baths. A. L.

An Additive Reaction of Nitriles. By ALEXANDER EIBNER and FR. A. SENF (*Ber.*, 1901, 33, 3549—3551).—The capacity of the cyanohydrins of alkylideneamines to take part in condensations with aldehydes in presence of potassium cyanide or alcoholic potash appears to be general (compare von Miller and Plöchl, *Abstr.*, 1896, i, 609) and extends to the cyanohydrins of hydrazones. With propylidenehydrazone cyanohydrin and benzaldehyde, the substance



is formed; this separates from light petroleum in rhombic tablets and melts at 123°. In this instance, the best results are obtained when the two substances are allowed to remain together for 24 hours in alcoholic solution without any condensing agent. A. L.

Action of Methylacetylacetone and Ethylacetylacetone on Diazochlorides. By G. FAVREL (*Compt. rend.*, 1901, 132, 41—42).—The action of methylacetylacetone on diazobenzene chloride yields a hydrazone, $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{COMe}$, which melts at 134° and seems to be identical with the compound obtained by von Pechmann by the action of phenylhydrazine on diacetyl and by Japp and Klingemann by the action of diazobenzene chloride on methylacetoacetic acid. Ethylacetylacetone yields the corresponding ethyl derivative, which melts at 117° and was likewise prepared by Japp and Klingemann. Diazo-*o*-tolyl and diazo-*p*-tolyl chlorides behave in a similar manner, whilst the bisdiazochlorides from benzidine and its homologues yield the dihydrazones of diacetyl or propionylacetyl, as the case may be. *Diacetyldiphenyldihydrazone* melts at 283 — 284° , and the corresponding propionylacetyl compound at 265 — 268° . C. H. B.

Stereoisomerism of the two Crotonic Acids. 4-Methylpyrazole-5-carboxylic Acid. By HANS VON PECHMANN and EMIL BURKARD (*Ber.*, 1901, 33, 3590—3594).—As in the interaction of methyl diazoacetate with methyl maleate and fumarate (Buchner, *Abstr.*, 1893, i, 431), identical products are obtained by the action of diazomethane on the methyl esters of crotonic and isocrotonic acids.

Methyl 4-methylpyrazoline-5-carboxylate, $\text{N} \begin{smallmatrix} \text{CH}\cdot\text{CHMe} \\ \text{NH}\cdot\text{CH}\cdot\text{CO}_2\text{Me} \end{smallmatrix}$, is a colourless syrup which decomposes on distillation. It is oxidised by

bromine to *methyl 4-methylpyrazole-5-carboxylate*, $\text{N} \begin{smallmatrix} \text{CH}\cdot\text{CMe} \\ \text{NH}\cdot\text{C}\cdot\text{CO}_2\text{Me} \end{smallmatrix}$, which melts at 170 — 171° , crystallises from dilute alcohol, dissolves in most solvents, and in dilute alkalis and mineral acids, but not in acetic acid; the *ethyl* ester melts at 156 — 158° ; the *acid*, $\text{C}_5\text{H}_6\text{O}_2\text{N}_2$, crystallises from water in small, glistening prisms, and melts at 218 — 220° . By distilling with soda-lime, the acid is converted into

4-methylpyrazole, $\text{N} \begin{smallmatrix} \text{CH}\cdot\text{CMe} \\ \text{NH}\cdot\text{CH} \end{smallmatrix}$, which boils at 204 — 205° under 730 mm. pressure, and differs in odour and in solubility from 3-methylpyrazole; the double salt, with *silver nitrate*, crystallises from hot water in glistening needles, and melts at 142° , that of the isomeride melting at 121° ; by the action of nitric acid, a yellow oil is produced, and not a crystalline nitro-compound; the *picrate*, like that of the isomeride, melts at 142° . T. M. L.

Pyrazole Derivatives from Diazomethane and Olefin monocarboxylic Acids. By HANS VON PECHMANN and EMIL BURKARD (*Ber.*, 1901, 33, 3594—3596).—By the action of diazomethane on methyl acrylate, methyl pyrazoline-3-carboxylate, $\text{N} \begin{smallmatrix} \text{NH}\cdot\text{CH}_2 \\ \text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me} \end{smallmatrix}$, is produced, and on oxidation and hydrolysis is converted into Buchner and Papendieck's 3-pyrazolecarboxylic acid (*Abstr.*, 1893, i, 431).

In a similar way, methyl cinnamate is converted into *methyl 5-phenylpyrazoline-4-carboxylate*, $\text{N} \begin{smallmatrix} \text{NH}\cdot\text{CHPh} \\ \text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me} \end{smallmatrix}$, which melts at 128° ,

crystallises in colourless prisms from alcohol, acetone, or benzene, and is insoluble in water. *Methyl 5-phenylpyrazole-4-carboxylate*,

$$\text{N} \begin{array}{c} \text{NH} \cdot \text{CPh} \\ \diagdown \quad | \\ \text{CH} \cdot \text{C} \cdot \text{CO}_2\text{Me} \end{array}$$
 prepared by the action of bromine on the preceding compound, crystallises from alcohol in small prisms and melts at $188-190^\circ$; the acid is identical with the 5-phenylpyrazole-4-carboxylic acid described by Knorr (Abstr., 1895, i, 396), and decomposes at its melting point into carbon dioxide and 5-phenylpyrazole. T. M. L.

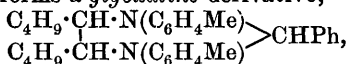
Combination of Diazomethane with Citraconic and Mesoconic Acids. By HANS VON PECHMANN and EMIL BURKARD (*Ber.*, 1901, 33, 3597—3598).—Esters of citraconic and mesaconic acids combine with diazomethane to form an ester of the same 5-methylpyrazoline-4 : 5-dicarboxylic acid, $\text{N} \begin{array}{c} \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ \diagdown \quad | \\ \text{NH} \cdot \text{CMe} \cdot \text{CO}_2\text{H} \end{array}$; by the action of bromine on this ester and subsequent hydrolysis, a mol. of carbon dioxide is eliminated, and 5-methylpyrazole-4-carboxylic acid,

$$\text{N} \begin{array}{c} \text{CH} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ \diagdown \quad | \\ \text{NH} \cdot \text{CMe} \end{array}$$
, is produced. T. M. L.

Pyrimidine from Barbituric Acid. By SIEGMUND GABRIEL (*Ber.*, 1900, 33, 3666—3668. Compare Abstr., 1899, 638).—Pyrimidine can be prepared more readily than from methyluracil by treating barbituric acid (malonylureide) with phosphorus oxychloride and reducing the resulting trichloropyrimidine. 2 : 4 : 6-*Trichloropyrimidine*, $\text{CH} \begin{array}{c} \text{CCl} \cdot \text{N} \\ \diagdown \quad | \\ \text{CCl} \cdot \text{N} \end{array} \text{CCl}$, is a heavy, colourless oil the vapour of which attacks the eyes; it boils at 213° under 755 mm. pressure, and after solidification melts at 21° . When heated with zinc dust and water, it is converted into pyrimidine. The yield amounts to about 16 per cent. of that calculated from the barbituric acid. A. H.

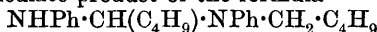
Conversion of Anil Compounds of *iso*Valeraldehyde into A. W. von Hofmann's corresponding Alkyl-substituted Ethylene Bases. By ALEXANDER EIBNER and GEORG PURUCKER (*Ber.*, 1900, 33, 3658—3664. Compare Abstr., 1892, 1189).—The base previously obtained by the reduction of *isovaleraldehyde*aniline with sodium and ethyl alcohol has the constitution of a *diisobutylethylene*aniline, $\text{C}_4\text{H}_9 \cdot \text{CH}(\text{NHPh}) \cdot \text{CH}(\text{NHPh}) \cdot \text{C}_4\text{H}_9$. It is not affected by boiling with concentrated hydrochloric acid, but condenses with ethylene bromide to form *diisobutyl**diphenyl**piperazine*, $\text{NPh} \begin{array}{c} \text{CH}_2 \text{---} \text{CH}_2 \\ | \quad \quad | \\ \text{CH}(\text{C}_4\text{H}_9) \cdot \text{CH}(\text{C}_4\text{H}_9) \end{array} \text{NPh}$, which crystallises in silky needles melting at 121° , and yields a *p-nitroso*-derivative crystallising in yellowish-green needles. The base also reacts with benzaldehyde to form a *glyoxaline* derivative, $\text{CHPh} \begin{array}{c} \text{NPh} \cdot \text{CH} \cdot \text{C}_4\text{H}_9 \\ | \quad \quad | \\ \text{NPh} \cdot \text{CH} \cdot \text{C}_4\text{H}_9 \end{array}$, which separates in tabular crystals melting at 109° . *iso*Valeraldehyde-*p*-toluidine is also converted by reduction with sodium and ethyl alcohol into an *ethylene* base, $\text{C}_2\text{H}_2(\text{C}_4\text{H}_9)_2(\text{NH} \cdot \text{C}_6\text{H}_4\text{Me})_2$, which is a thick, colourless oil boiling at about 270° . The *hydrochloride*

crystallises in white plates, and the *diacetyl* derivative in vitreous monoclinic tablets melting at 138° , whilst the *monobenzoyl* derivative forms thin plates melting at 156° . The *dinitrosoamine*, $C_{24}H_{34}O_2N_4$, crystallises in pale yellow needles or cubes, melts at 92° , and is not affected by treatment with alcoholic hydrogen chloride. With benzaldehyde, the base forms a *glyoxaline* derivative,

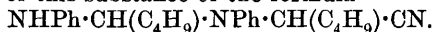


which crystallises in large tablets melting at 154° .

In the reduction of *isovaleraldehydeaniline* to *diisobutylethyleneaniline*, an intermediate product of the formula



is probably formed, and the mononitrile previously obtained by the action of dilute hydrocyanic acid on *isovaleraldehydeaniline* appears to be a derivative of this substance of the formula

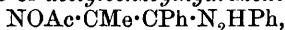


On reduction with sodium and ethyl alcohol, it yields the *ethyleneaniline*, whilst on distillation it yields the original base and the simpler nitrile.

A. H.

1:3-Diphenyl-4-methylosotriazole. By GIACOMO PONZIO and P. ROSSI (*Gazzetta*, 1900, 30, ii, 454—458).—This compound has been prepared by removing a molecule of acetic acid from the acetyl derivative of β -acetylbenzoylhydrazoxime by means of sodium carbonate.

The *acetyl* derivative of *acetylbenzoylhydrazoxime*,



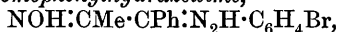
crystallises from alcohol in faintly yellow prisms melting at 134.5° .

1:3-Diphenyl-4-methylosotriazole, $\begin{array}{c} CMe \cdot N \\ CPh : N \end{array} > NPh$, separates from

alcohol in almost colourless prisms melting at 37.5 — 38° , and is soluble in the cold in the ordinary organic solvents, but insoluble in water. The *dinitro*-derivative, $C_{15}H_{11}N_3(NO_2)_2$, crystallises from acetic acid in prisms melting at 230 — 231° . The *tetranitro*-compound separates from acetone in yellow prisms melting at 172° .

1-p-Bromophenyl-3-phenyl-4-methylosotriazole, $C_2N_3MePh \cdot C_6H_4Br$, crystallises from alcohol in slender, white needles melting at 97° .

Acetylbenzoyl-p-bromophenylhydrazoxime,



separates from alcohol in yellowish needles melting at 206 — 207° .

1-p-Iodophenyl-3-phenyl-4-methylosotriazole crystallises from alcohol in sparkling laminae melting at 106° , and on treating with nitric acid yields the *dinitrodiphenylmethylosotriazole* melting at 230 — 231° .

T. H. P.

Oxidation of Hydrazoximes. V. By GIACOMO PONZIO (*Gazzetta*, 1900, 30, ii, 459—465).—**2-Methyl-3:n-diphenyl-1:2-oxypyrrro-1:4-diazole** [4:5-oxo-1:3-diphenyl-4-methylosotriazole], $O < \begin{array}{c} CMe \\ N \cdot NPh \cdot N \end{array} \begin{array}{c} CPh \\ N \end{array}$, ob-

tained by oxidising β : α -acetylbenzoylhydrazoxime in chloroform solution by means of mercuric oxide, crystallises from light petroleum in shining, faintly yellow needles melting at 83° , and is soluble in all ordinary organic solvents. It does not yield a hydrochloride when

hydrogen chloride is passed through its ethereal solution, but on reduction either in alcoholic solution with zinc and hydrochloric acid, or with hydriodic acid in sealed tubes, it gives 1:3-diphenyl-4-methylsotriazole. Its dinitro-compound separates from acetic acid in microscopic, yellowish prisms melting at 260°, and is soluble in acetone, benzene, or chloroform.

Triphenyl-1:2-oxypyrrro-1:4-diazole [4:5-oxo-1:3:4-triphenylosotriazole], $O < \begin{array}{c} \text{CPh} \text{---} \text{CPh} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{NPh} \cdot \text{N} \end{array}$, prepared by oxidising benzylhydrazoxime

in chloroform solution with mercuric oxide, crystallises from acetone in aggregates of yellowish needles melting at 169°, and is soluble in benzene and slightly so in light petroleum or alcohol. By the action of zinc and hydrochloric acid in alcoholic solution, or of hydriodic acid in a sealed tube at 140°, it is converted into triphenylosotriazole, the hexanitro-compound of which, $\text{C}_{20}\text{H}_9\text{N}_3(\text{NO}_2)_6$, separates from acetic acid in shining, yellow prisms melting at 205—206°, and is almost insoluble in all other organic solvents. T. H. P.

6-Methylxanthine. By MARTIN KRÜGER (*Ber.*, 1900, 33, 3665. Compare Abstr., 1898, i, 699; 1899, ii, 233).—The 6-methylxanthine previously isolated from human urine readily yields theophylline (4:6-dimethylxanthine) on methylation, the latter being isolated by precipitating its sodium salt with sodium hydroxide in the cold. 6-Methylxanthine is best crystallised from acetic acid, and separates in very thin, six-sided, rhombic plates. A. H.

Azo-compounds Derived from *m*-Toluidine. By S. SAMELSON (*Ber.*, 1900, 33, 3479—3483).—The following azo-compounds were prepared by combining dimethyl-*m*-toluidine with diazotised bases. *Dimethyl-m-toluidineazobenzene*, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N}_2\text{Ph}$, obtained by using aniline, crystallises from alcohol in lustrous, bright-red needles, melts at 66°, and yields a dark-brown, amorphous *platinichloride*, which sinters at 200°, but does not melt at 280°.

The *sulphonic acid*, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, obtained with sulphanilic acid, is a reddish-brown, hygroscopic powder which is sparingly soluble in water, softens at 210°, carbonises at 225°, and yields a *barium salt* in the form of lustrous, brown crystals; on reduction, the acid gives sulphanilic acid and *p*-aminodimethyl-*m*-toluidine.

Dimethyl-m-toluidine-azo-p-toluene, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Me}$, prepared with *p*-toluidine, crystallises from alcohol in lustrous, bright red needles, and melts at 121°; the *hydrochloride* crystallises from alcohol and melts at 172°; the *platinichloride* is a dark-red, amorphous powder, whilst the *sulphate* separates in greenish needles from methyl alcohol and melts at 201°.

Dimethyl-m-toluidineazo-m-toluene, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Me}$, from *m*-toluidine, separates from alcohol in scarlet crystals, melts at 73—74°, and yields a brown, amorphous *platinichloride* which carbonises at 197°.

Dimethyl-m-toluidineazo-p-phenetole, obtained by using *p*-phenetidine, forms small, brown crystals and melts at 136—137°; the *platinichloride*, a bluish-grey, amorphous powder, carbonises at 197°.

Dimethyl-m-toluidineazo-p-anisole, separates from alcohol in reddish-brown crystals, melts at $135-136^{\circ}$, and yields a blue, crystalline *hydrochloride* melting at 164° which dissolves in alcohol to a red solution; the *sulphate* crystallises from methyl alcohol in dark blue needles and melts at 198° , and the *platinichloride* is amorphous and decomposes at 202° .

W. A. D.

isoDiazotisation of Arylamines. By EUGEN BAMBERGER and ERNST RÜST (*Ber.*, 1900, 33, 3511—3512. Compare Abstr., 1894, i, 511).—Aromatic bases, when diazotised in alkaline solution, that is, with amyl nitrite and sodium ethoxide, yield *isodiazotates* and no trace of the normal compounds. That the *iso*-compound is not a secondary product obtained by the action of sodium ethoxide on diazoaminobenzene has been proved by the fact that these compounds do not react on one another. Aniline, *o*- and *p*-toluidine, *p*-chloroaniline *p*-bromoaniline all react in a similar manner, but mesidine appears to be incapable of yielding an *isodiazotate*. Methylamine and benzylamine do not react, nor can phenylnitroamine be obtained by the action of amyl nitrate and sodium ethoxide on aniline. J. J. S.

Action of Nitrosobenzene on Aromatic Hydrazines. By EUGEN BAMBERGER (*Ber.*, 1900, 33, 3508—3510. Compare Abstr., 1900, i, 193, and Spitzer, this vol., i, 98).—According to the author, molecular quantities of nitrosobenzene and *s*-diphenylhydrazine react in hot alcoholic solution to give a quantitative yield of azobenzene and β -phenylhydroxylamine. Nitrosobenzene and phenylhydrazine yield diazohydroxylaminobenzene and phenylhydroxylamine. *p*-Tolylhydrazine and nitrosobenzene give *p*-toluenediazohydroxylaminobenzene, $C_6H_4Me \cdot N \cdot N \cdot NPh \cdot OH$, melting at $130-131^{\circ}$ and phenylhydroxylamine, *p*-nitrosotoluene, and phenylhydrazine yield benzenediazohydroxylamino-*p*-toluene, $NPh \cdot N \cdot N(OH) \cdot C_6H_4Me$, melting at $123.5-124^{\circ}$ and *p*-tolylhydroxylamine. J. J. S.

Arylthiolsulphonates and Arylsulphinates of Diazo-compounds. By JULIUS TROEGER and ERICH EWERS (*J. pr. Chem.*, 1900, [ii], 62, 369—430).—When benzidine or tolidine is diazotised, and the cold, neutral solution treated with a solution of the potassium salt of a thiolsulphonic acid, the corresponding thiolsulphonate of the diazo-compound is immediately precipitated. The products thus obtained sometimes undergo a remarkable transformation; for example, the benzene- and *p*-toluene-thiolsulphonates of bisdiazodiphenyl and bisdiazoditolyl separate in well-defined crystals which, when kept, lose their crystalline structure and become amorphous. The products obtained when diazo-compounds are treated with the salts of sulphinic acids are, however, always amorphous. The substances, both from thiolsulphonates and from sulphinates, are all of a golden- or orange-yellow colour. The thiolsulphonates cannot be purified by recrystallisation, since decomposition readily occurs with evolution of nitrogen; some of the products obtained with sulphinates dissolve in cold ethyl acetate or chloroform, and can be reprecipitated by means of light petroleum. When heated with aniline or nitrobenzene, solution of either series of compounds is effected with simultaneous evolution of the nitrogen, and this reaction has been employed for the estimation

of the nitrogen. All the salts of diazo-compounds described in this paper yield a carmine red coloration with alcoholic potassium hydroxide.

By the action of thiolsulphonates on bisdiazodiphenyl chloride, the following salts were obtained. *Bisdiazodiphenyl dibenzenethiolsulphonate*, $C_{12}H_8(N_2 \cdot S \cdot SO_2Ph)_2$, decomposes at $129-130^\circ$, the *di-p-toluenethiolsulphonate* at 147° , the *di-o-toluenethiolsulphonate* at 140° , and the *di- α - and - β -naphthalenethiolsulphonates* at 125° and $131-133^\circ$ respectively.

The following compounds were prepared by the addition of thiolsulphonates to solution of bisdiazoditolyl chloride. *Bisdiazoditolyl dibenzenethiolsulphonate* decomposes at about 132° ; of the *di-o-* and *-p-toluenethiolsulphonates*, the latter decomposes at $135-136^\circ$; *di- α - and - β -naphthalenethiolsulphonates* decompose at 108° and 112° respectively.

By the action of sulphinites on the diazo-compounds as well in acid as in neutral solution, the following sulphones were obtained: *diphenylsulphonebisdiazodiphenyl*, $C_{12}H_8(N_2 \cdot SO_2Ph)_2$, and the corresponding *di-o-* and *-p-tolyl-*, *di- α - and - β -naphthyl-*, and the *dibromophenyl-sulphones*. *Diphenylsulphonebisdiazoditolyl* decomposes at 119° , the corresponding *di-o-* and *-p-tolylsulphones* decompose at 119° and 128° , and the *di- α - and - β -naphthylsulphones* at 130° and 128° respectively; the *dibromophenyl-sulphone* decomposes at 128° .

The arylthiolsulphonates of diazo-compounds, derived from primary amines, are comparatively stable and indifferent towards acids and alkalis. When kept, they sometimes decompose spontaneously with evolution of nitrogen; a similar decomposition occurs on heating. They react with alkaline phenol solutions with formation of oxyazo-compounds and the alkali salts of the thiolsulphonic acids. The thiolsulphonates of these diazo-compounds are nearly insoluble in water, but more or less soluble in alcohol, ether, chloroform, or carbon disulphide; as the substances dissolve, decomposition occurs, and hence the original products cannot be recovered from their solutions. The compounds are obtained both amorphous and crystalline; many solutions yield at first oily precipitates which gradually harden, whilst a further quantity afterwards separates in leaflets or needles; some products are at first crystalline and soluble in water, but after a time become amorphous and insoluble. The colour of these substances is yellow, orange, red, or brown.

The following compounds were prepared by the action of thiolsulphonates on diazobenzene chloride. *Diazobenzene benzenethiolsulphonate*, $Ph \cdot N_2 \cdot S \cdot SO_2Ph$, decomposes at 75° ; if its solution in carbon disulphide is treated with alcohol and evaporated by means of a current of air, a yellow, crystalline residue is obtained, which consists of a mixture of diazobenzenepherylsulphone and diazobenzene benzenethiolsulphonate. *Diazobenzene p-toluenethiolsulphonate* decomposes at $88-89^\circ$, the *α -naphthalenethiolsulphonate* melts and decomposes at $95-96^\circ$, and the *β -naphthalenethiolsulphonate* decomposes at $79-80^\circ$.

The following salts result from the action of thiolsulphonates on *p*-diazotoluene chloride. *p-Diazotoluene benzenethiolsulphonate*, $C_6H_4Me \cdot N_2 \cdot S \cdot SO_2Ph$, melts and decomposes at 80° , the *p-toluenethiolsulphonate* decomposes at 93° , the *α -naphthalenethiolsulphonate* decomposes at 115° , and the *β -naphthalenethiolsulphonate* melts and decomposes at 92° .

o-Diazotoluene benzenethiolsulphonate melts at 52° and decomposes at

about 55°; the *p*-toluenethiolsulphonate melts and decomposes at 79°; the α -naphthalenethiolsulphonate decomposes at 86.5°, and the β -naphthalenethiolsulphonate melts and decomposes at 92.5°.

The compounds obtained by the action of potassium benzene- and *p*-toluene-thiolsulphonates on *m*-diaz-o-xylene chloride are extremely unstable. *m*-Diaz-o-xylene α - and β -naphthalenethiolsulphonates melt and decompose at 98—99° and 87—88° respectively; both these compounds readily react with alkaline resorcinol with formation of *m*-xyleneazo-resorcinol.

Diazo- ψ -cumene benzenethiolsulphonate, $C_6H_2Me_3 \cdot N_2 \cdot S \cdot SO_2Ph$, melts and decomposes at 73°, the *p*-toluenethiolsulphonate melts and decomposes at 87°, the α -naphthalenethiolsulphonate softens at 52—53°, and melts and decomposes at 90—91°, and the β -naphthalenethiolsulphonate decomposes at 85°; the last-mentioned compound reacts with alkaline resorcinol in the cold with formation of ψ -cumeneazoresorcinol, and when warmed with alkaline phenol solution yields ψ -cumeneazophenol.

α -Diazonaphthalene benzenethiolsulphonate, $C_{10}H_7 \cdot N_2 \cdot S \cdot SO_2Ph$, melts and decomposes at 90—91°, the *p*-toluenethiolsulphonate decomposes at 97°, and the α -naphthalenethiolsulphonate decomposes at 108°; the β -naphthalenethiolsulphonate melts and decomposes at 101—102°, and reacts with alkaline solution of resorcinol with formation of α -naphthaleneazoresorcinol.

β -Diazonaphthalene benzenethiolsulphonate decomposes at 87°; the *p*-toluenethiolsulphonate melts and decomposes at 104°; and the α -naphthalenethiolsulphonate decomposes at 115—116°; the β -naphthalenethiolsulphonate softens at 55°, decomposes at 95—96°, and reacts with alkaline solution of phenol with formation of β -naphthaleneazophenol.

o-Chlorodiazobenzene benzenethiolsulphonate melts and decomposes at 87—88°; the *p*-toluenethiolsulphonate decomposes at 89—90°; the α - and β -naphthalenethiolsulphonates are extremely unstable, and could not be obtained in a pure, dry state. The corresponding *m*- and *p*-chloro-compounds were prepared.

p-Bromodiazobenzene benzenethiolsulphonate decomposes at 99—100°; the *p*-toluenethiolsulphonate melts and decomposes at 111°; the α -naphthalenethiolsulphonate melts at 105—106°, and the β -naphthalenethiolsulphonate melts and decomposes at 108—109°.

m-Bromodiazobenzene benzenethiolsulphonate melts at 60°, and decomposes at 80°; the *p*-toluene- and α - and β -naphthalene-thiolsulphonates could not be obtained in a pure, dry state.

p-Nitrodiazobenzene benzenethiolsulphonate melts and decomposes at 113°; the *p*-toluenethiolsulphonate melts and decomposes at 116°, and when warmed with alkaline solution of resorcinol yields *p*-nitrobenzene-azoresorcinol; the α -naphthalenethiolsulphonate decomposes at 58°, and the β -naphthalenethiolsulphonate melts and decomposes at 127°.

m-Nitrodiazobenzene benzenethiolsulphonate melts and decomposes at 109—110°; the *p*-toluenethiolsulphonate decomposes at 92—93°; both the α - and β -naphthalenethiolsulphonates soften at 50° and decompose at 56—57°.

The thiolsulphonates of *o*-nitrodiazobenzene are very unstable; only the α -naphthalenethiolsulphonate could be obtained in a pure state.

p-Diazoisole benzenethiolsulphonate, $OMe \cdot C_6H_4 \cdot N_2 \cdot S \cdot SO_2Ph$, melts

at 70—71° and decomposes at 73°; the *p*-toluenethiolsulphonate melts and decomposes at 102—103°; the α -naphthalenethiolsulphonate melts and decomposes at 100—101°, and the β -naphthalenethiolsulphonate decomposes at 91·5°; the three last-mentioned substances react with alkaline solution of resorcinol, with formation of *p*-anisoleazoresorcinol.

o-Diazobenzene benzenethiolsulphonate melts and decomposes at 73°; the *p*-toluenethiolsulphonate melts and decomposes at 82°; the α -naphthalenethiolsulphonate melts and decomposes at 95—96°, and the β -naphthalenethiolsulphonate decomposes at 92°.

p-Diazophenetole benzenethiolsulphonate, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{S} \cdot \text{SO}_2\text{Ph}$, melts and decomposes at 81—82°; the *p*-toluenethiolsulphonate melts and decomposes at 116°; the α - and β -naphthalenethiolsulphonates melt and decompose at 121° and 122° respectively, and react with alkaline resorcinol solution with formation of *p* phenetoleazoresorcinol.

Diazoazobenzene benzenethiolsulphonate, $\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{S} \cdot \text{SO}_2\text{Ph}$, melts and decomposes at 120°; the *p*-toluenethiolsulphonate melts and decomposes at 114°, and the α - and β -naphthalenethiolsulphonates melt and decompose at 117·5° and 116·5° respectively.

The stability of the thiolsulphonates of the diazo-compounds is largely dependent on the nature and position of the substituting radicles in the benzene nucleus. Negative atoms or groups, such as Cl, Br, NO_2 , increase the stability if they enter the para-position to the diazo-group, whilst, on the other hand, if they occupy the meta-position, the products are less stable. The thiolsulphonates of *m*-nitrodiazobenzene are less easily decomposed than those of *m*-chloro- and *m*-bromo-diazobenzene, for whilst the salts of *m*-nitrodiazobenzene could all be obtained in a pure, dry state, in the case of the *m*-chloro- and *m*-bromo-diazobenzene only the benzenethiolsulphonate could be prepared.

Among the ortho-compounds, the thiolsulphonates of *o*-nitrodiazobenzene are less stable than those of *o*-chlorodiazobenzene; the α -naphthalenethiolsulphonate of *o* nitrodiazobenzene was with difficulty obtained in a pure state, and the product decomposed within 12 hours; the benzene- and *p*-toluene-thiolsulphonates of *o*-chlorodiazobenzene can be kept for months without change, whilst its naphthalenethiolsulphonates rapidly decompose.

The naphthalenethiolsulphonates of diazo-compounds substituted in the ortho- or meta-position by negative radicles are the most unstable, whilst the benzenethiolsulphonate is the most stable.

The entrance of a methyl group into the benzene nucleus of the diazo-compound increases the stability of the thiolsulphonate; the naphthalenethiolsulphonates of such compounds are more stable than the *p*-toluene- and benzene-thiolsulphonates; the thiolsulphonates of *p*-diazotoluene are all somewhat more stable than the corresponding diazobenzene compounds. The benzene- and *p*-toluene-thiolsulphonates of *o*-diazotoluene can only be obtained with difficulty, and rapidly decompose, whilst the α - and β -naphthalenethiolsulphonates are readily prepared in a pure state.

The thiolsulphonates of diazo- ψ -cumene can all be obtained pure, but the benzene- and *p*-toluene-thiolsulphonates are the least stable.

Since the thiolsulphonates of the diazo-compounds can, in many

cases, be kept for months without change, they rather resemble the diazo-sulphones than the unstable diazo-chlorides, -nitrates, and -sulphates.

The behaviour of many of these compounds points to the existence of two modifications; for example, the β -naphthalenethiolsulphonate of *p*-diazotoluene, the *p*-toluenethiolsulphonate of α -diazonaphthalene, the benzenethiolsulphonate of β -diazonaphthalene, and the β naphthalenethiolsulphonate of *p*-chlorodiazobenzene are for a short time after their formation soluble in water and crystalline, and on drying pass into insoluble, amorphous modifications. Many substances are at first crystalline, and become resinous when dry; for example, the α - and β -naphthalenethiolsulphonates of β -diazonaphthalene and *m*-chlorodiazobenzene; with some of the benzenethiolsulphonates of diazo-compounds containing a halogen in the meta- or ortho-position, this change takes place so rapidly that the formation of the crystalline modification can only be observed with difficulty. The existence of these two modifications can be explained by means of the stereoisomeric formulæ suggested by Hantzsch (Abstr., 1894, i, 455). E. G.

Proteids of the Thymus Gland. By CORNELIS A. PEKELHARING and HUISKAMP (*Proc. K. Acad. Amsterdam*, 1900, 3, 383—386).—Hammarsten has shown that fibrin cannot be regarded as a calcium compound of fibrinogen. This, however, does not alter the views held by the present authors regarding the nature of the fibrin-ferment; but recent work on the thymus proteids confirms it. Two nucleo-proteids can be separated from aqueous extracts of thymus. One of these (Lilienfeld's nucleo-histon) is quite insoluble, the other is incompletely soluble in water containing from 0.1 to 0.5 per cent. of calcium chloride; by increasing the amount of calcium salt, or by adding other neutral salts, both dissolve readily.

The precipitates produced from thymus extract by the addition of the necessary amount of calcium chloride are to be considered as calcium salts, in which the nucleo-proteid plays the part of an acid. By treatment of these compounds with potassium oxalate, the potassium compound of nucleo-proteid is formed. The potassium nucleo-proteid, like the sodium and ammonium compound, is soluble in water. The magnesium and barium compounds are insoluble in water, but dissolve in ammoniated water. All these compounds of nucleo-histon are precipitated by the addition of so much salt that the fluid contains 0.9 of sodium chloride, 1.13 of potassium chloride, 0.1 of calcium chloride, and 0.2 of magnesium sulphate per cent. respectively. Elementary analyses of the calcium compounds of the two nucleo-proteids gave the following percentages: Calcium nucleo-histon: Ca, 45.3; H, 6.5; N, 17.1; P, 3.75; S, 0.51; Ca, 1.34. Calcium nucleo-proteid: C, 49.8; H, 7.3; N, 15.9; P, 0.95; S, 1.19; Ca, 1.34.

Both these calcium proteids can act as fibrin-ferment, but this action is influenced by the amount of calcium salt in solution as well, being most effective in fibrin formation when the solution contains from 0.1 to 0.5 per cent. of calcium chloride. Beyond this, no coagulation occurs. Horne has previously shown that the chlorides of calcium, barium, and strontium, when present to an extent exceeding 0.5

per cent., hinder blood coagulation. The same is true for the fibrin-ferment prepared from blood. If fresh blood is mixed with calcium chloride, so that 1 per cent. of that salt is present, it remains fluid but clots on dilution, and clots best when the percentage amount of calcium salt in solution is 0.25 per cent., that is, in the strength in which the calcium nucleo-proteids are least soluble. W. D. H.

The Influence of Various Substances on the Crystallisation of Hæmoglobin. By STANISLAUS VON STEIN (*Virchow's Archiv*, 1900, 162, 477—487).—The experiments were performed on the blood of the guinea-pig, and the author's Canada balsam method of preparing crystals was used. Various reagents, such as distilled water, sodium chloride, potassium chloride, &c., were added to the blood, and in all cases beyond a certain limit (the numbers are given in detail) the addition finally prevents crystallisation. An interesting point noticed is that, with a certain percentage addition of sodium and potassium salts, the crystals obtained are principally six-sided plates instead of tetrahedra. W. D. H.

Antipeptone and Amphopeptone. By MAX SIEGFRIED (*Ber.*, 1900, 33, 3564—3568. Compare this vol., i, 57).—The greater part of the paper is a reply to Kutscher's criticisms (this vol., i, 108). Fibrin or Witte's peptone, digested with pepsin in the presence of hydrochloric or sulphuric acid, yields two monobasic acids, $C_{21}H_{34}O_9N_6$, and $C_{21}H_{36}O_{10}N_6$; these substances give the biuret reaction and are strongly acidic, yielding salts on boiling with zinc oxide or barium carbonate. G. T. M.

Chemical Composition of the Brain Tissue. By EMIL WÖRNER and HANS THIERFELDER (*Zeit. physiol. Chem.*, 1900, 30, 542—551).—The following substances have been obtained from brain tissue by extraction with a mixture of benzene and alcohol or chloroform and alcohol at 45—50°.

1. *Cerebron* (C = 69.16, H = 11.54 and N = 1.76 per cent.) separates first; it forms perfectly white characteristic amorphous, nodular masses, does not contain phosphorus, and is insoluble in water, but dissolves in most organic solvents; when heated in a capillary tube, it becomes moist at about 130° and melts at 209—212°. When warmed with 85 per cent. alcohol at 50°, the rounded masses become transformed into well-defined hexagonal plates; this transformation is accompanied by an addition of water. It forms an amorphous bromo-derivative, and when warmed with hydrochloric acid reduces Fehling's solution owing to the formation of galactose.

2. A compound containing 56.1—56.5 per cent. of carbon and melting and decomposing at about 270°. It is characterised by the property it possesses of melting when warmed with alcohol containing benzene.

3. A substance crystallising in rosettes of small needles and having all the appearance of "protagon"; it is probable that this is a mixture. J. J. S.

Myrosin. By THOMAS BOKORNY (*Chem. Zeit.*, 1900, 24, 817 and 832. Compare Abstr., 1900, ii, 746).—Some *Cruciferae* contain both myrosin

and potassium myronate (or a glucoside yielding allylthiocarbimide, others contain myrosin alone with no corresponding glucoside, whilst in some cases neither is present. No instance has as yet been observed of the occurrence of potassium myronate without myrosin; the statement of Spatzier (*Pr. Journ.*, 1893, 25) that this is the case with *Capsella bursa pastoris* (Shepherd's purse) is erroneous. Bussy (*Journ. Pharm.*, 26, 39) prepared myrosin by extracting mustard seed with cold water, evaporating at 40° to a syrup, and repeatedly precipitating with alcohol; the author finds, however, that the activity of myrosin is destroyed by 50 per cent. aqueous alcohol, whilst on drying expressed radish-juice, even at 25°, no active ferment can be obtained.

The action of myrosin is destroyed by a 5 per cent. formaldehyde solution, but not by a 1 per cent. solution, whilst a solution of the strength 1:10,000 is fatal to protoplasm. The fermenting power of myrosin is destroyed by 1 per cent. sulphuric acid, 0.1 per cent. silver nitrate solution, or 0.1 per cent. mercuric chloride solution, whilst hydroxylamine is without action. In presence of water, the ferment loses its power at 70—75°, protoplasm under the same conditions being killed at 50—60°.

T. H. P.

Sensitiveness of Enzymes; their relation to Protoplasm. By THOMAS BOKORNY (*Chem. Zeit.*, 1900, 24, 1113—1114; 1136—1138).—A parallel is drawn between enzymes and the protoplasm of lower organisms with respect to the action on both of poisons, temperature, or strong illumination. Some facts are tabulated that illustrate the parallelism.

C. F. B.

Action of Enzymes on Chromatophores and Dissolved Dyes. By C. J. KONING (*Chem. Centr.*, 1900, ii, 1279—1280; from *Pharm. Weekbl.*, 1900, No. 21, 23, 24).—The death of organisms resulting from the destruction of the protoplasm, but in which an enzyme still remains active, is named necrobiose. The change of colour of the dying leaves of *Isatis tinctoria* is due to the action of the enzyme isatase on isatan, which is an unstable indoxyl compound. In order to preserve the natural colour of plants, such as, for instance, *Campanula rotundifolia*, the plant must be heated at a higher temperature to insure necrose or the destruction of both protoplasm and enzyme. The enzymes may also act as catalytic agents and in cases of necrobiose the glucosides are often decomposed by the action of the enzymes. The action of the colouring matters which accompany chlorophyll is also described more particularly in reference to carotin and anthocyanin.

E. W. W.

Vegetable Oxidases. By B. SLOWTZOFF (*Zeit. physiol. Chem.*, 1900, 31, 227—234).—Laccase loses its activity at high temperatures; its action is proportional to the square root of its quantity. The amount of the product obtained is a function of the quantity of ferment, not of the quantity of the oxidisable substance. The action goes on best in the presence of a slightly alkaline reaction. In composition and reactions, laccase is a proteid; it is, however, not destroyed by acids or by peptic or pancreatic digestion.

W. D. H.

Lipase, the Fat-splitting Enzyme, and the Reversibility of its Action. By J. H. KASTLE and A. S. LOEVENHART (*Amer. Chem. J.*, 1900, **24**, 491—525).—The authors have employed ethyl butyrate to determine the activity of solutions of lipase, since it is much more rapidly hydrolysed than fats by this enzyme. The most convenient source of lipase is the pancreas of the pig, but it can also be obtained from other tissues, the lipolytic activity of which stand in the following ratio: pancreas, 1.0; liver, 2.93; kidney, 0.50; sub-maxillary gland, 0.36. Since the liver of the pig showed such remarkable activity, it was compared with the livers of the ox, sheep, chicken, and duck; in a series of parallel experiments, the liver of the pig hydrolysed 8.66 per cent. of the ethyl butyrate employed, that of the sheep 4.77, that of the duck 2.70, that of the ox 2.20, and that of the chicken 1.95 per cent. The extract of the stomach of the pig was found to possess lipolytic activity in neutral solution, but was rendered permanently inactive by free hydrochloric acid in the quantity normally present in the gastric juice. Lipase also occurs in the small intestine of the pig, the mucous lining of which possesses a lipolytic activity equal to three-fourths of that of the fresh pancreas.

Lipase is much more stable than is usually supposed; it hydrolyses ethyl butyrate most rapidly at 40°, and at 65—70° the enzyme is destroyed. It is almost completely removed from its solutions by repeated filtration through paper. The behaviour of lipase towards ethyl formate, ethyl acetate, ethyl propionate, and ethyl butyrate was studied; it was found that the higher the molecular weight of the ester, the more readily is it hydrolysed by lipase, whilst the converse is true for the hydrolysis of esters by acids.

The effect of several of the commoner antiseptics on lipase was examined; it is shown that such substances as silver nitrate, mercuric chloride, salicylic acid, and osmic acid are much more detrimental than the more feeble antiseptic substances, such as toluene, chloroform, and thymol; sodium fluoride, hydrofluoric acid, and acids generally are particularly harmful.

The rate of hydrolysis, in the case of the extract of the pig's liver, is directly proportional to the concentration of the enzyme, but independent of the concentration of the ester; the reaction is not complete in ordinary circumstances, but if the extract of lipase is very concentrated and the ester present in only small quantity, the hydrolysis approaches completion. The velocity of the reaction is not constant, but diminishes as the hydrolysis proceeds.

The authors have found that the synthesis of ethyl butyrate from butyric acid and alcohol can be effected by means of lipase, thus proving that the hydrolysis of an ester by this enzyme is a reversible reaction. The paper concludes with a discussion of the relation of this fact to the absorption of fat in the animal organism and the translocation of fatty reserve materials in plants. E. G.

Ptyalin Activity. By T. MASZEWSKI (*Zeit. physiol. Chem.*, 1900, **31**, 58—64).—In the first series of experiments, equal quantities of saliva, and equal volumes of starch paste, were taken, but the amount

of starch in the paste was variable. The amount of sugar formed increased with the increase in the amount of starch.

In the second series, the volume of starch paste was the variable quantity. The amount of sugar formed increased with the volume of the starch solution.

In the third series, the volume of the saliva was the variable quantity. Here the amount of sugar formed hardly varied at all; there was often a slight decrease in the amount of sugar formed, never an increase.

In the light of such experiments, the faultiness of methods used for the estimation of enzymes is revealed.

W. D. H.

Tannase. By AUG. FERNBACH (*Compt. rend.*, 1900, 131, 1214—1215).—*Aspergillus niger*, a mould which plays an important part in the industrial processes of gallic fermentation, yields, when macerated with cold water, a solution which promotes the hydrolysis of tannin. This extract, when concentrated in a vacuum and treated as in Lintner's preparation of amylase, yields a grey powder containing the tannin ferment *tannase*. Tannin dissolved in 10 parts of water is completely hydrolysed by a solution of this enzyme; the course of the fermentation is readily followed by means of the polarimeter, the rotation of the solution becoming *nil* when the action is completed. The same transformation is effected by the action of a tannase solution, passed through a Chamberland filter, on a sterilised solution of tannin.

G. T. M.

Tannase; a Diastase decomposing Gallotannic Acid. By HENRI POTTEVIN (*Compt. rend.*, 1900, 131, 1215—1217. Compare preceding abstract).—Spores of *Aspergillus niger* are cultivated at 30° in Raulin's liquid, containing tannin instead of sucrose, until the mycelium begins to fructify; the mould is then washed and macerated in the dark with chloroform and water, the extract being passed through a Chamberland filter. Sterilised solutions of tannin are completely hydrolysed by the filtrate, but no action takes place if the tannase is destroyed by heating the solution to boiling. Variable quantities of dextrose are produced, together with gallic acid, during fermentation. *Aspergillus niger*, cultivated in the ordinary Raulin's liquid, does not yield tannase unless the sugar of the solution is replaced by gallic acid or tannin.

Phenyl and methyl salicylates are hydrolysed by tannase, and since they have a constitution similar to that proposed by Schiff for digallic acid, these results go to confirm the suggested formula. Tannase also hydrolyses tannates such as gelatin tannate; the ferment is in all probability widely distributed in nature and has been found in sumach leaves; this accounts for the fact that gallic acid always accompanies tannin.

G. T. M.

Zymase from Sterilised Yeast. By EDUARD BUCHNER (*Ber.*, 1900, 33, 3307—3310. Compare Abstr., 1897, ii, 380).—Washed and pressed bottom yeast was dried for 3 or 4 hours at temperatures from 35° to 100° under 30 mm. pressure, and was then sterilised by heating in hydrogen

for several hours at temperatures varying from 98° to 110°. The material thus obtained, which was incapable of development in beer wort, was mixed with glycerol and water, and ground with sand and kieselguhr. The juice expressed from this mass possessed active fermentative powers, 20 c.c. of it when mixed with 8 grams of cane sugar yielding, on the average, about 0.5 gram of carbon dioxide. Similar results were obtained with yeast dried in the air and then heated at 97° in a current of carbon dioxide. The author regards this result as decisive against the view that the fermentative powers of expressed yeast juice are due to the presence of fragments of living protoplasm in the juice, since, in his experiments, no living protoplasm could be present.

It was observed that thoroughly dried yeast was extremely difficult to sterilise, and sometimes withstood heating at 100° for 8 hours.

A. H.

Simple Experiment to illustrate the Action of Zymase. By ROBERT ALBERT (*Ber.*, 1900, 33, 3775—3778).—Fresh brewery yeast is freed from water by pressing, and rubbed through a sieve into a mixture of absolute alcohol and ether (3:1). After 4—5 minutes, the liquid is poured off, the residue drained, washed with ether, and spread out in a thin layer on filter-paper to dry. A yellowish-white powder is obtained, which contains no live yeast cells, but ferments sugar solution vigorously.

The zymase is contained within the dead cells, and cannot be extracted with water directly. To obtain a fairly strong solution of it, the powder is rubbed with very fine quartz sand in a large mortar, water then added, and the mixture rubbed for 10 minutes more. It is then filtered with the aid of a pump through hardened filter-paper, some of the dilute zymase solution precipitated with alcohol and ether, the powder so obtained dissolved in a little water, a little kieselguhr added, and filtered. The clear filtrate so obtained ferments cane sugar almost instantaneously, even at the ordinary temperature.

C. F. B.

Invertase from Yeast. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1900, 31, 305—328. Compare KÖlle, *Abstr.*, 1900, i, 572).—Invertase obtained by Barth's method (*Ber.*, 1878, 11, 474) always contains an appreciable amount of yeast-gum (*Abstr.*, 1894, i, 222, 316; 1895, i, 166), which can be isolated in the form of its copper sodium derivative. Four different specimens examined contained from 17.17 to 65.3 per cent. of this gum. The gum, on hydrolysis, yields *d*-mannose (Hessenland), and this is probably the origin of the mannose obtained by Osborne and by KÖlle from so-called invertase. Contact with alcohol appears to rapidly destroy the hydrolytic power of diastase. The isolation of "sucrase," the actual enzyme of cane sugar inversion from yeast in a pure form by any of the ordinary methods, appears to the author to be hopeless, on account of the large number of other enzymes present, namely, maltase, zymase, and the three enzymes previously described by him (*Zeit. physiol. Chem.*, 1889, 13, 506).

J. J. S.

Organic Chemistry.

Hydrogenation with Sodium and Alcohol. By ALBERT LADENBURG (*Ber.*, 1901, **34**, 200—201. Compare von Baeyer, *Ber.*, 1900, **33**, *Sonderheft*, p. 57).—A claim for priority in the use of sodium and alcohol for hydrogenation, as, for example, in the reduction of pyridine to piperidine. T. M. L.

Hydrocarbon, C_6H_{10} , from Dimethylallylcarbinol. By EUGEN LJUBARSKY (*J. pr. Chem.*, 1900, **62**, [ii], 567—577).—The hydrocarbon, C_6H_{10} , first obtained by Saytzeff (*Abstr.*, 1877, ii, 298) from dimethylallylcarbinol, is a colourless, mobile liquid which boils at $73-76^\circ$, exhibits a slight violet-blue fluorescence, and has the sp. gr. 0.71427 at $20^\circ/0^\circ$, 0.71504 at $20^\circ/20^\circ$, and 0.71415 at $20^\circ/4^\circ$, and a molecular refraction 50.34. It absorbs oxygen from the air with formation of a thick, yellow oil. By the action of hypochlorous acid on the hydrocarbon, a pale yellow liquid, probably the dichlorohydrin, is obtained, which is converted by barium hydroxide into a thick, colourless liquid of the composition $C_6H_{10}O(OH)_2$. The author concludes that the hydrocarbon is *as-methylallylethylene* [β -methyl- $\alpha\delta$ -pentadiene],
 $CH_2 \cdot CH \cdot CH_2 \cdot CMe \cdot CH_2$. E. G.

cyclopentadiene Dibromides. By JOHANNES THIELE (*Annalen*, 1901, **314**, 296—310. Compare Kraemer and Spilker, *Abstr.*, 1896, i, 289; and Thiele, *Abstr.*, 1900, i, 2).—According to the author's hypothesis, the dibromide of *cyclopentadiene* should have the constitution of a 1:4-derivative, $CH_2 \begin{smallmatrix} \swarrow CHBr \cdot CH \\ \searrow CHBr \cdot CH \end{smallmatrix}$, and not of a 1:2-derivative, $CH_2 \begin{smallmatrix} \swarrow CHBr \cdot CHBr \\ \searrow CH=CH \end{smallmatrix}$.

Examination of the behaviour of the hydrocarbon towards bromine has shown that two stereoisomeric 1:4-dibromides are formed. Each yields a dibromodihydroxycyclopentene when oxidised with potassium permanganate, chromic acid converting the glycols into $\alpha\gamma$ -dibromoglutaric acids, having to one another the relation which racemic acid bears to mesotartaric acid. The $\alpha\gamma$ -dibromoglutaric acids may be reduced to glutaric acid, showing that the hydrocarbon is a *cyclopentadiene*, and not a methylcycloetradiene.

trans-cyclopentadiene dibromide is the crystalline derivative described by Kraemer and Spilker (*loc. cit.*); when reduced with zinc dust and glacial acetic acid, it yields the hydrocarbon. *cis-cyclopentadiene dibromide*, conveniently obtained by treating the hydrocarbon with bromine dissolved in chloroform, is a colourless, refractive oil, which soon becomes turbid when exposed to light and air, liberating hydrogen bromide; it boils at $53-54^\circ$ under 2 mm. pressure, and has a sp. gr. 1.9443 at $14^\circ/4^\circ$.

trans-1:4-Dibromo-2:3-dihydroxycyclopentane, $CH_2 \begin{smallmatrix} \swarrow CHBr \cdot CH \cdot OH \\ \searrow CHBr \cdot CH \cdot OH \end{smallmatrix}$

prepared by oxidising the *trans*-dibromide in alcohol with potassium permanganate at 0°, crystallises from benzene in small, hard prisms, and melts at 75·5°; the *di*-*p*-nitrobenzoyl derivative, $C_{19}H_{14}O_8N_2Br_2$, crystallises from toluene in yellowish needles and melts at 158—159°.

Racemic α -dibromoglutaric acid, $CH_2(CHBr\cdot CO_2H)_2$, obtained on oxidising the *trans*-glycol with chromic acid, crystallises in white needles or leaflets which melt and decompose at 142—143°.

cis-1 : 4-Dibromo-2 : 3-dihydroxycyclopentane, $CH_2 \begin{matrix} \text{CHBr} \cdot \text{CH} \cdot \text{OH} \\ \text{CHBr} \cdot \text{CH} \cdot \text{OH} \end{matrix}$

formed when the liquid dibromide is oxidised with potassium permanganate, crystallises from benzene in small, white needles, and melts at 76—77°; the *di*-*p*-nitrobenzoyl derivative crystallises in yellowish aggregates and melts at 147—148°.

Inactive α -dibromoglutaric acid, obtained by oxidising the glycol with chromic acid, is identical with the product obtained by directly brominating glutaric acid. M. O. F.

Derivatives of cyclopentadiene. By JOHANNES THIELE (*Ber.*, 1901, 34, 68—71).—cyclopentadiene, unlike indene, is very readily acted on in benzene solution by potassium, giving a potassium derivative which forms a yellow powder, is insoluble in benzene, inflames spontaneously in the air, is decomposed immediately by water, and reacts with halogen compounds and with carbon dioxide; the potassium derivative is not formed when the hydrocarbon is dissolved in light petroleum, or below 15°. Bis-cyclopentadienecarboxylic acid, $(C_5H_5\cdot CO_2H)_2$, prepared by the action of dry carbon dioxide on the potassium derivative, crystallises from acetic acid in tablets or short prisms, melts at 210°, is only slightly soluble in hot water, is not readily acted on by sodium hydroxide or sodium amalgam, but is decomposed by heating above the melting point, and immediately decolorises alkaline permanganate. The dimethyl ester, $C_{14}H_{16}O_4$, crystallises from light petroleum in needles and melts at 85°, has a normal molecular weight in chloroform solution, is readily hydrolysed by alcoholic potash, and by distillation is converted into the ester of the unimolecular acid, which gradually polymerises to the crystalline bimolecular ester.

The tetrabromide of the dimethyl ester, $C_{14}H_{16}O_4Br_4$, separates from ethyl acetate as a white, crystalline powder, begins to decompose at 140°, and melts at about 180—185°. T. M. L.

Action of Heptylic Alcohol on its Sodium Derivative. New Method for the Synthesis of Alcohols. By MARCEL GUERBET (*Compt. rend.*, 1901, 132, 207—210. Compare Abstr., 1899, i, 471, 472).—Heptylic alcohol, when heated at 220° in contact with its sodium derivative, undergoes a condensation similar to that effected in the case of inactive amyl alcohol. The main reaction may be thus formulated, $2C_7H_{16}O + C_7H_{15}ONa = C_7H_{13}O_2Na + C_{14}H_{30}O$, the products being sodium heptoate and a new alcohol derived from 2 mols. of heptylic alcohol by the elimination of 1 mol. of water.

β -Diheptylic alcohol, $C_{14}H_{29}OH$, is a colourless liquid with a faint odour, boiling at 151·5—152·5° under 13 mm., and at 286—289° under ordinary pressure, and having a sp. gr. 0·8405 at 15°.

A secondary reaction results from the further condensation of 2 mols. of the preceding compound with 1 mol. of sodium heptyl-oxide, $2C_{14}H_{30}O + C_7H_{16}ONa = C_{21}H_{44}O + C_{14}H_{27}O_2Na + 4H$. The alcoholic product, *triheptylic alcohol*, $C_{21}H_{43}OH$, a colourless, almost odourless liquid, boils at $202-206^\circ$ under 13 mm. pressure, and has a sp. gr. 0.8447 at 15° . The acidic product, $C_{13}H_{27}CO_2H$, is isomeric with myristic acid and Perkin's diheptoic acid, and is termed β -*diheptoic acid*; it melts at 4° , and boils at $190-191^\circ$ under 13 mm. pressure.

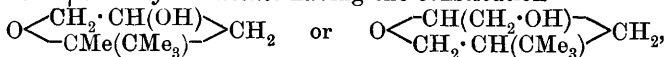
G. T. M.

Methylisopropylallylcarbinol. By GEORG WAGNER, jun. (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 794-797).—*Methylisopropylallylcarbinol*, $C_3H_5 \cdot CMePr^s \cdot OH$, prepared by the action of zinc on a mixture of methylisopropyl ketone (1 mol.) and ethyl iodide (1.5 mols.), is a colourless, mobile liquid with a faint turpentine-like odour, and is insoluble in water; it boils at 155.6° under 760 mm. pressure, and has the sp. gr. 0.85059 at $20^\circ/0^\circ$ and 0.85168 at $20^\circ/20^\circ$. When oxidised with potassium permanganate solution, it yields the corresponding *tri-hydroxy-compound*, $OH \cdot CMePr^s \cdot CH_2(OH) \cdot CH_2 \cdot OH$, which is a syrupy liquid, very soluble in water or alcohol, but only slightly so in ether; its *triacetyl* derivative, $C_{14}H_{24}O_6$, formed, together with a small proportion of the diacetyl derivative, when the trihydroxy-compound is heated in a sealed tube with acetic anhydride, is a viscous liquid, readily soluble in alcohol or ether, but only slightly so in water.

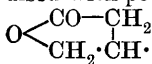
T. H. P.

Action of Sulphuric Acid on the Trihydroxy-compound obtained by the Oxidation of Methyltertbutylallylcarbinol. By ALEXANDER PETCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 780-794).—By the oxidation of methyltertbutylallylcarbinol with potassium permanganate, a trihydric alcohol of the composition $OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot CMe(OH) \cdot CMe_3$ is obtained. The action of sulphuric acid on this alcohol gives rise to the two products:

(1) The γ -oxide of an alcohol having the constitution



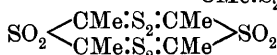
which is a viscous liquid with a faintly camphor-like smell and a cooling, caustic taste, and boils without decomposition at $214-215^\circ$; it has the sp. gr. 0.9837 at $0^\circ/0^\circ$, 0.9699 at $20^\circ/0^\circ$, 0.9716 at $20^\circ/20^\circ$, 0.96998 at $20^\circ/4^\circ$, n_D 1.45447, and its molecular refraction indicates the absence of a double linking in the molecule. The *acetyl* derivative, $C_{11}H_{20}O_2$, has been prepared and analysed. When the γ -oxide is oxidised with potassium dichromate and sulphuric acid, it yields a γ -lactone,



which crystallises from ether in large, quadratic plates melts at $96-98^\circ$, resolidifies at $84-82^\circ$, and dissolves readily in alcohol, but less so in water. On neutralising aqueous solutions of the lactone with baryta, lime or potassium hydroxide, *barium*, *calcium*, or *potassium* salts of an acid of the composition $C_8H_{16}O_3$ are obtained. The γ -lactone may be prepared directly by the action of sulphuric acid on β -methyltertbutylhydracrylic acid.

(2) An oily product which is insoluble in water, and is found to be a mixture of two ethers derived from the trihydric alcohol, one, $C_{18}H_{34}O_3$, by the removal of 3 mols. of water from 2 of the alcohol, and the other, $C_{18}H_{36}O_4$, by the removal of 2 mols. of water from 2 of the alcohol. Oxidation of the mixture with 1 per cent. aqueous potassium permanganate gives rise to the crystalline γ -lactone melting at $96-98^\circ$. T. H. P.

Ethenyltrisulphide [Tetraethenyl Hexasulphide] and its Derivatives. By EMIL FROMM and GEORG MANGLER (*Ber.*, 1901, 34, 204—217).—The sulphide, $C_4H_6S_3$, prepared by Bongartz (Abstr., 1886, 1000) by the action of zinc chloride on thioacetic acid, and the sulphone, $C_4H_6O_2S_3$, formed from it by oxidation, are shown by molecular weight determinations to have the double formulæ $C_8H_{12}S_6$ and $C_8H_{14}O_4S_6$; the names *tetraethenyl hexasulphide* and *tetraethenyldisulphonet etrasulphide*, and the formulæ $S \begin{smallmatrix} \text{CMe:S}_2\text{:CMe} \\ \text{CMe:S}_2\text{:CMe} \end{smallmatrix} S$ and

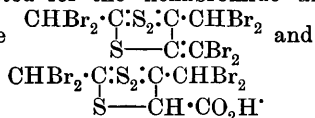


are therefore proposed. The sulphide is stable towards alkalis, alkyl haloids, and acetic anhydride, and the disulphone is not oxidised further by chromic acid or by nitric acid.

By the action of bromine on a solution in chloroform of the hexasulphide, a *hexabromotrisulphide*, $C_6H_2Br_6S_3$, is produced, apparently by the elimination of one acetyl residue and three atoms of sulphur from the hexasulphide; it dissolves in 700 parts of boiling alcohol, crystallises on cooling in long, white, silky needles, and is readily soluble in chloroform, benzene, or carbon disulphide. Sodium methoxide or potassium hydroxide in methyl alcoholic solution converts the hexabromide into the *orthotrimethyl ester*, $C_5H_3Br_4S_3 \cdot C(OMe)_3$, of a carboxylic acid; the ester forms tabular crystals, melts at $125-126^\circ$, and explodes at higher temperatures, does not lose methyl alcohol when heated at 82° or when boiled with chloroform or with alcohol, but is readily converted by methyl alcoholic sulphuric acid into the *monomethyl ester*, $C_5H_3Br_4S_3 \cdot CO_2Me$, which crystallises from methyl alcohol, melts at $146-147^\circ$, decomposes at a slightly higher temperature, and has the normal molecular weight for the above formula. The *acid*, $C_5H_3Br_4S_3 \cdot CO_2H$, crystallises from methyl alcohol or from water in long, pointed needles, begins to decompose at 130° , but when rapidly heated melts and explodes at 162° . The *ammonium* salt separates in minute needles and melts at $193-194^\circ$.

By the action of sodium ethoxide on the hexabromide, the *monoethyl ester*, $C_5H_3Br_4S_3 \cdot CO_2Et$, is produced, but the orthotriethyl ester could not be obtained; the ethyl ester crystallises from alcohol in bulky aggregates of needles, melts at $115-116^\circ$, and is readily hydrolysed by alkalis to the carboxylic acid.

The formulæ suggested for the hexabromide and the carboxylic acid derived from it are



T. M. L.

Iodination by means of Chloride and Bromide of Iodine. By WLADIMIR ZERNOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 804—819).—By the action of a mixture of iodine and bromine on glacial acetic acid in presence of red phosphorus, iodoacetic acid is formed, but no bromoacetic acid.

α-Iodoisovaleric acid, $C_5H_9O_2I$, obtained by the action of a chloroform solution of iodine monochloride (1 mol.) on a mixture of phosphorus pentachloride (1 mol.) and *isovaleric acid* (1 mol.), separates from light petroleum in nodules or from a mixture of acetone and benzene in aggregates of long, transparent prisms melting at 52° ; it is readily soluble in the organic solvents but only slightly so in water, and its aqueous or alcoholic solution can be titrated with sodium hydroxide solution with phenolphthalein as indicator. The *sodium*, with aq.?, *silver*, *copper*, with $2H_2O$, *barium*, with $4H_2O$, and *zinc* salts have been prepared. On heating a sodium hydroxide solution of the iodo-acid, it is converted into *α-hydroxyisovaleric acid*, together with a small quantity of an unsaturated compound, whilst when the acid is added to boiling 15 per cent. sodium hydroxide solution, the main product is dimethylacrylic acid, the hydroxy-acid being formed only in small proportion.

α-Iodobutyric acid, $C_4H_7O_2I$, crystallises from a mixture of benzene and light petroleum in stout needles which melt at $41\text{--}42^\circ$ and are readily soluble in alcohol, acetone, ether, or light petroleum, but only slightly so in water. On heating a solution of its sodium salt, the acid is converted into *α-hydroxybutyric acid*. T. H. P.

Simple and Mixed Acid Anhydrides. By WILHELM AUTENRIETH [and, in part, J. KOBURGER and PAUL SPIESS] (*Ber.*, 1901, 34, 168—187).—When a fatty acid is boiled for 4—6 hours with 2—3 times its weight of acetic anhydride, a mixture of the simple and mixed anhydrides of the acid is obtained; the simple anhydride is generally the principal product, and the proportion of it increases with the amount of acetic anhydride employed and with the time of heating. The mixed anhydrides do not boil as constantly as the simple anhydrides, but the extent of their decomposition during distillation is not so great as hitherto supposed; only on heating for several hours under pressure at $200\text{--}220^\circ$ is the decomposition very marked, and even then it is not complete, owing to a condition of equilibrium being established.

The author has confirmed experimentally his original statement (*Abstr.*, 1888, 250) that, when mixed anhydrides interact with phenylhydrazine, the hydrazide of the acid containing the greater amount of carbon is formed; this statement has recently been contradicted by Béhal (*Abstr.*, 1900, i, 8), who explained the formation of *isovalerylphenylhydrazine* from acetic *isovaleric* anhydride and phenylhydrazine by assuming the latter to interact with the *isovaleric acid* formed owing to the production of acetylphenylhydrazine. It is now shown that fatty acids, contrary to Béhal's statements (*Ann. Chim. Phys.*, 1900, [vii], 19, 284), yield at the ordinary temperature with phenylhydrazine, either alone or dissolved in ether, only salts of the base and not acylhydrazines; acetic acid yields the acetate only and *isovaleric acid*

the *isovalerate* (m. p. 40—43°). The salts, moreover, do not change with time into acylhydrazines [Leighton (Abstr., 1899, i, 50) finds the reverse], and the latter are only formed by loss of water when the temperature is raised to 80—90°.

With phenols, mixed anhydrides yield nearly equal quantities of the two possible acyl derivatives, and the same is true of alcohols, although Béhal asserts that only one is formed in quantity.

The following compounds are new :—*Acetic butyric anhydride* boils at 155—175°; with aniline (2 mols.) it yields butyranilide almost exclusively, and with phenylhydrazine, butyrylphenylhydrazine (m. p. 103°; Schmidt, Abstr., 1889, 1159, gives 113—114°, and Vahle, Abstr., 1894, i, 411, 103°).

Acetic isovaleric anhydride when pure boils at 175—181°, and is more mobile than *isovaleric anhydride*, which boils at 203—208°. The former yields, with phenylhydrazine, *isovalerylphenylhydrazine* almost exclusively which melts at 110—111°, not at 101° as formerly stated; when boiled with phenol for 2 hours, the anhydride yields phenyl acetate and *phenyl isovalerate*, a colourless, aromatic, heavy oil which boils at 224—226° (uncorr.). *isoValeric acid* does not act on phenol under similar conditions.

n-Hexoic anhydride, $(C_6H_{11}O)_2O$, is the principal product obtained from hexoic acid and boils at 242—245°; with warm aqueous ammonia, it yields *n-hexoamide*, which crystallises in white, nacreous leaflets and melts at 98°.

n-Octoic anhydride boils at 280—285°, and with phenylhydrazine yields *n-octoylphenylhydrazine*, which crystallises from alcohol in lustrous leaflets and melts at 102—104°.

With acetic anhydride, aromatic acids readily yield the simple anhydrides; the latter are the principal products and are much more stable in contact with cold aqueous sodium carbonate than the mixed anhydrides, advantage being taken of this to effect purification. Benzoic anhydride is only dissolved by 10 per cent. aqueous sodium carbonate after boiling for $\frac{3}{4}$ hour. *m-Nitrobenzoic anhydride* crystallises from dilute alcohol in needles, melts at 47°, with ammonia yields *m-nitrobenzamide*, and with phenylhydrazine the *m-nitrobenzoyl* derivative.

m-Bromobenzoic anhydride was not obtained pure, but its action with ammonia and phenylhydrazine is apparently normal; *m-bromobenzoylphenylhydrazine* crystallises from dilute alcohol in slender, colourless needles and melts at 152°.

Cinnamic acid yields an oily mixture of anhydrides which ultimately deposits crystals of cinnamic anhydride; with ammonia, the latter yields cinnamamide (m. p. 147°, Rossum, *Zeit. Chem.*, 1866, 362, gives 141·5°), and with aniline and phenylhydrazine the corresponding anilide and phenylhydrazide.

W. A. D.

Undecenoic Acid. By HERMANN THOMS and GEORG FENDLER (*Arch. Pharm.*, 1900, 238, 690—699).—When undecenoic acid (obtained by distilling castor oil) is oxidised by permanganate in the cold, α -dihydroxyundecenoic acid is not the only product; indeed, it is formed only in relatively small amount, the chief product being sebacic acid. When undecenoic acid (1 mol.) is oxidised with less than 1 mol. of permanganate

at 0° , there is formed, in addition to sebacic acid, a κ -hydroxy- ι -keto-undecic acid, which is soluble in benzene, melts at 90 — 103° , losing water meanwhile, and then has the composition $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{H}$. The potassium salt of this acid and its semicarbazone and acetate (melting at 145° and 111 — 112° respectively) were prepared; the acid is oxidised to sebacic acid, either by mercuric oxide, bromine, or hydrogen peroxide; when it is treated with potassium cyanide and hydrochloric acid, sebacic acid is again formed. C. F. B.

Electrolysis of Hydroxy-acids: Preparation of β -Amyloxypropionic Acid and the Diamyl Derivative of Butylene Glycol. By JULES HAMONET (*Compt. rend.*, 1901, 132, 259—261).—The alkali salts of the β -alkyloxy-acids are readily electrolysed in accordance with the equation $2\text{OR}\cdot\text{C}_n\text{H}_m\cdot\text{CO}_2\text{K} = \text{K}_2 + 2\text{CO}_2 + \text{OR}\cdot\text{C}_n\text{H}_m\cdot\text{C}_n\text{H}_m\cdot\text{OR}$, but the α -derivatives under the same conditions are to a large extent hydrolysed.

β -Amyloxypropionic acid, a colourless liquid which boils at 145 — 146° and at 251 — 252° under pressures of 15 and 750 mm. respectively, and has a sp. gr. 1.051 at 18° , is readily obtained from its *amyl* ester, a liquid boiling at 140° and 259 — 260° under pressures of 20 and 750 mm. respectively, and of sp. gr. 0.901 at 18° . The *amyl* ester is obtained by the action of sodium amyloxide in presence of *amyl* alcohol on *amyl β -chloropropionate*, which is obtained by the usual method, and is a colourless liquid with a fruity odour, of sp. gr. 1.024 at 18° , and boiling at 109 — 110° under 21 mm. pressure.

The *diamyl derivative of butylene glycol*, $\text{C}_4\text{H}_8(\text{O}\cdot\text{C}_5\text{H}_{11})_2$, an oily liquid of sp. gr. 0.849 at 18° and boiling at 260 — 261° under 750 mm. pressure, is obtained by the electrolysis of a solution of potassium β -amyloxypropionate with a current of about 2 amperes. C. H. B.

Wandering of Acyl Groups. By WILHELM WISLICENUS and HEINRICH KORBER (*Ber.*, 1901, 34, 218).—The conversion of ethyl O-acetylacetoacetate, $\text{CMe}(\text{OAc})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, into ethyl diacetoacetate, $\text{CHAc}_2\cdot\text{CO}_2\text{Et}$, takes place when the ester is heated at 200° , as well as under the influence of alkalis (Claisen and Haase, this vol., i, 118), as is shown by the production of acetylacetone. A similar change has been observed by Claisen in the case of the O-benzoate of dibenzoylmethane. T. M. L.

Complex Salts of Platinum. (IV.) Oxalonitrites of the Alkaline Earth Metals. By MAURICE VÉZES (*Bull. Soc. Chim.*, 1901, [iii], 25, 157—165. Compare Abstr., 1898, i, 64; 1899, i, 671, 741).—*Barium platoso-oxalonitrite*, $\text{Pt}(\text{C}_2\text{O}_4)(\text{NO}_2)_2\cdot\text{Ba}\cdot 5\text{H}_2\text{O}$, is obtained by mixing cold, concentrated solutions of mol. proportions of barium chloride and potassium platoso-oxalonitrite, in the form of golden-yellow crystals having the appearance of elongated parallelograms. It becomes anhydrous at about 200° , and decomposes at about 275° with the formation of oxides of nitrogen, platinum, and barium oxalate or carbonate. It is soluble in 40 parts of cold, or 10 parts of boiling, water; the solutions decompose slowly in the cold, and more quickly on boiling, barium oxalate being precipitated.

Barium potassium platoso-oxalonitrite, $\text{Pt}_2(\text{C}_2\text{O}_4)_2(\text{NO}_2)_4\cdot\text{BaK}_2\cdot 4\text{H}_2\text{O}$, obtained in the same manner as the preceding compound, but using

half the amount of barium chloride, crystallises in brownish-yellow prisms. It becomes anhydrous on heating, and finally decomposes at about 250° with the formation of oxides of nitrogen, platinum, and barium and potassium oxalates. Compounds analogous to those described are probably formed by calcium and strontium, but their instability has hitherto prevented their isolation. N. L.

Synthesis of Fumaric Acid from Glyoxylic and Malonic Acids. By OSCAR DOEBNER (*Ber.*, 1901, 34, 53—55).—Glyoxylic acid, which frequently occurs in plants, condenses with malonic acid in presence of pyridine at 100° , and fumaric acid results by the loss of a molecule of carbon dioxide. It is suggested that glyoxylic acid, like formaldehyde, is an important intermediate product in the formation of polybasic vegetable acids. T. M. L.

Formaldehyde as a Product of the Incomplete Combustion of Carbon Compounds. By S. P. MULLIKEN, J. W. BROWN, and P. R. FRENCH (*Amer. Chem. J.*, 1901, 25, 111—117. Compare this vol., ii, 43).—Loew's apparatus was employed for estimating the amount of formaldehyde produced when different carbon compounds are incompletely oxidised.

As acetaldehyde interferes with the estimation of formaldehyde, it must be removed by boiling the aqueous solution in an apparatus provided with a reflux condenser filled with water at 45 — 50° . Only minute traces of formaldehyde are thus lost.

Acetone gave 0.22; ethyl alcohol, 0.44; pentane, 0.88; acetic acid, 0.84; ether, 1.86; amylene, 2.01; *n*-propyl alcohol, 2.72; and trimethylcarbinol, 5.17 per cent. of formaldehyde. J. J. S.

Action of Sodium Hydroxide on α -Hydroxyisobutaldehyde. By ADOLF FRANKE (*Monatsh.*, 1900, 21, 1122—1132).—All the aliphatic aldehydes hitherto investigated, except formaldehyde, have given aldols under the influence of alkalis; aromatic aldehydes, on the other hand, under similar conditions, are converted quantitatively into the corresponding alcohol and acid (Cannizzaro's reaction).

α -Hydroxyisobutaldehyde (Abstr., 1900, i, 427) contains no hydrogen attached to the α -carbon atom, and therefore cannot give an aldol; it is now shown that, under the influence of warm sodium hydroxide solution, it yields β -methylpropyleneglycol (Wagner, Abstr., 1888, 665) and α -hydroxyisobutyric acid, and thus reacts in the same way as aromatic aldehydes. α -Bromoisobutaldehyde yields the same products when warmed with alkali. J. J. S.

Composition of a Wood Oil. By GEORGE S. FRAPS (*Amer. Chem. J.*, 1901, 25, 26—53).—The author has investigated the composition of a wood oil obtained by the distillation of hard-wood tar; after the crude product had been treated with potassium hydroxide, it was redistilled. The brownish-red oil thus obtained was carefully fractionated.

From the fractions distilling below 140° , sodium hydrogen sulphite removed methyl ethyl ketone, valeraldehyde, methyl *n*-propyl ketone, cyclopentanone, and methyl *n*-butyl ketone; mesityl oxide was not present. The residues from this treatment were dried with potassium carbonate

and hydrolysed with aqueous sodium hydroxide; a small quantity of ammonia was produced indicating the presence of nitriles, whilst methyl alcohol was found in the alkaline solution. The esters present were methyl acetate, propionate, *n*-butyrate, valerate, and probably α - and β -crotonates, together with small quantities of esters of organic acids of higher molecular weight than valeric acid. The oils undissolved by the sodium hydroxide were dried and fractionated; the fraction boiling below 70° yielded 2-methylfurfuran, but dimethylacetal was not present; phenylhydrazine combined with a portion of the oil, and the product yielded small quantities of diethyl and other ketones. The residue, after the removal of the esters and ketones, contained neither alcohols nor pyridines, but furnished dimethyl- and trimethyl-furfuran, together with toluene, *m*-xylene, and small quantities of unsaturated compounds.

The fractions of the oil boiling between 140° and 210° were treated with sodium hydrogen sulphite, and yielded small quantities of aldehydes and ketones. Hydrolysis with sodium hydroxide indicated the presence of methyl *n*-valerate and hexoate. Creosote was also obtained together with a small proportion of furfurans higher than trimethyl-furfuran; phenol ethers were probably present in small quantities. The oils of higher boiling point, freed from ketones, aldehydes, esters, and creosote, were separated into two parts by glacial acetic acid, one soluble, the other insoluble; both absorbed bromine readily. E. G.

Density Expansion and Capillarity of Aqueous Sucrose Solutions. By J. DOMKE and H. HARTING [with F. PLATO] (*Zeit. Ver. deut. Zuckerind.*, 1900, 982—1015 and 1079—1102).—Numerous exact measurements have been made of these constants, the results being collected in tables. The following are the values of the sp. grs. of sucrose in various conditions: in solution, 1.55626 at 15°/15° and 1.5549 at 15°/4°; crystalline, 1.59103 at 15°/15° and 1.5897 at 15°/4°; crystallised (sugar candy), 1.5892 at 15°/15° and 1.5879 at 15°/4°; amorphous, 1.5090 at 15°/15° and 1.5077 at 15°/4°.

The authors find that sucrose is hygroscopic, and in air, saturated with water vapour, takes up as much as 1 per cent. of its weight of water, which it loses mostly at the ordinary temperature and completely at 90° in air of medium humidity. T. H. P.

Octabenzoylraffinose. By F. STOLLE (*Zeit. Ver. deut. Zuckerind.*, 1901, 33).—The octabenzoyl ester of raffinose, $C_{18}H_{25}O_{16}Bz_8$, prepared by the Schotten-Baumann method, separates from acetic acid as a crystalline powder melting at 98°. A glacial acetic acid solution containing 0.6596 gram of the ester in 50 c.c. gave a rotation of +4.1 sugar degrees in a 200 mm. tube at 18.6°. T. H. P.

Synthesis of Disaccharides. By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Sitzungsber. Akad. Wiss. Berlin*, 1901, 7, 123—131).—*Acetylchlorogalactose*, a colourless syrup produced by gently heating in sealed tubes a mixture of dry galactose and acetic chloride, decomposes on heating at 50°, reduces warm Fehling solution and is hydrolysed by water, slowly in the cold and more rapidly on warming. The substance is readily soluble in the ordinary organic solvents excepting

light petroleum and in alcoholic solution undergoes decomposition with the production of hydrogen chloride and ethyl acetate; it closely resembles its analogue acetylchloroglucose (Ryan, Trans., 1899, **75**, 1055).

A disaccharide is produced by mixing together in cold alcoholic solution either of these acetylchlorohexoses with the sodium derivative of a hexose, and subsequently hydrolysing the acetyl compound first produced by the addition of cold sodium hydroxide solution; in no case has a solid product been isolated, but the aqueous solution of the condensation product has been employed in fermentation experiments and in the preparation of crystalline osazones.

Phenylgalactosidoglucosazone, a pale yellow mass of microscopic needles, melts at 155—157° corr. and dissolves in 110 parts of boiling water, crystallising from this medium and also from ethyl acetate. When produced by the action of phenylhydrazine, 50 per cent. acetic acid, and sodium chloride on a warm dilute solution of the crude disaccharide, the new compound is always mixed with the less soluble osazones of dextrose and galactose, and is separated from these by fractional crystallisation from water.

Phenylglucosidogalactosazone crystallises from benzene, toluene, or water in pale yellow needles melting at 175—177° corr.; it is somewhat less soluble than the preceding compound, requiring for solution 120 parts of boiling water.

Phenylgalactosidogalactosazone dissolves in 110 parts of hot water and crystallises in pale yellow needles melting at 176—178° corr.; it readily dissolves in alcohol, ethyl acetate, acetone, or pyridine.

Pure cultures of "bottom" yeast have no fermenting action on galactosidogalactose, but slowly destroy the other two disaccharides; the three compounds, however, are practically not affected by "top" yeast, and hence this agent serves to separate these condensation products from the monosaccharides employed in their formation.

The solutions of the disaccharides, freed in this way from hexoses, were submitted to the action of emulsin and kephir lactase; the former enzyme hydrolyses the new compounds just as it decomposes lactose and melibiose, the latter hydrolyses glucosidogalactose only, the others remaining unaffected.

Since it seems possible for enzymes to bring about the formation of disaccharides from hexoses (Hill, Trans., 1898, **73**, 634) a mixture of galactose and dextrose was treated with an extract of kephir ferment, and after remaining for three months at 30° yielded an osazone readily soluble in water or toluene, crystallising in yellow needles, melting at 193—196° corr. and closely resembling phenyllactosazone.

G. T. M.

Amino-acids. By HANS MEYER (*Monatsh.*, 1900, **21**, 913—948).—The acidity of an amino-acid depends on the electrochemical character of the groups near to the amino-nitrogen atom; when this, or the carbon atom to which it is linked, is united to positive groups, the amino-acid has a neutral or only faintly acid reaction, as, for example, in the primary and alkyl-substituted aliphatic amino-acids, piperidine-carboxylic and pyrrolidinecarboxylic acids and betaines; when it is united to negative groups, the amino-acid reacts as a true acid, for

example, in such compounds as methyleneglutamine, aromatic amino-carboxylic acids and pyridinecarboxylic and quinolinecarboxylic acids. Substitution of an amino-hydrogen atom by alkyl in an aromatic amino-acid slightly decreases the acid reaction. The stability of the esters is, as a rule, the opposite of that of the acids—a stable acid, such as glycine, forming a very unstable ester; those acids in which the basic function of the amino-group is neutralised by the presence of a negative group are stable and form stable esters, whilst those in which the α -carbon atom is united to strongly negative groups are unstable, but form stable esters. All acid imides are hydrolysed by one equivalent of an alkali to the neutral salt of an amino-acid.

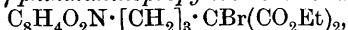
The following alkyl-substituted anthranilic acids were prepared by the action of the alkyl iodides on an aqueous solution of potassium anthranilate: *ethylanthranilic acid*, which crystallises in colourless, long needles and melts at 152–153°; *n-propylanthranilic acid*, which crystallises in greenish, flat needles and melts at 110°; *isobutylanthranilic acid*, which crystallises in colourless, long needles and melts at 84°; *isoamylanthranilic acid*, which crystallises in colourless, long needles and melts at 68–70°.

R. H. P.

Glycine. By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1900, **31**, 389–394. Compare this vol., i, 30).—When glycine is boiled with potassium hydroxide solution for several hours, only small quantities of ammonia and acetic acid are formed. Glycine reacts with sodium hypobromite, although little or no nitrogen is evolved; that a complex change has taken place is proved by the fact that the whole of the nitrogen is found in the precipitate obtained with phosphotungstic acid, whereas glycine itself yields no precipitate with this reagent. The nitrogen in the precipitate is mainly liberated as ammonia on boiling with concentrated potash, and formic acid is obtained when the alkaline residue is acidified and distilled.

J. J. S.

Synthesis of $\alpha\delta$ -Diaminovaleric Acid. By EMIL FISCHER (*Sitzungsber. Akad. Wiss. Berlin*, 1900, **52**, 1111–1121; *Ber.*, 1901, **34** 454–464).—*Ethyl γ -phthaliminopropylbromomalonate*,



obtained by the action of bromine on diethyl γ -phthaliminopropylmalonate, crystallises in prisms or plates, melts at 51° (corr.), and is decomposed in the cold by alkalis; when treated with ammonia, and then with hydrochloric acid, it yields phthalic acid and α -pyrrolidinecarboxylic acid, which, when treated with phenylcarbimide, forms *phenylcarbimino-2-pyrrolidinecarboxylic acid*,

$\text{CH}_2 \begin{matrix} \text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ \text{CH}_2 \cdot \text{N} \cdot \text{CO} \cdot \text{NHPh} \end{matrix}$; this crystallises from acetone, melts at about 170°, and is then converted into the inner *anhydride*, $\text{CH}_2 \begin{matrix} \text{CH}_2 \cdot \text{CH} \cdot \text{CO} \\ \text{CH}_2 \cdot \text{N} \cdot \text{CO} \end{matrix} \text{NPh}$, which crystallises in colourless prisms and melts at 118° (corr.).

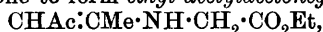
γ -Phthaliminopropylbromomalonate, obtained from the ester by hydrolysis with hydrogen bromide, crystallises with 2H₂O, and decomposes at about 140–145° with the formation of δ -phthalimino α -bromovaleric acid, $\text{C}_8\text{H}_4\text{O}_2\text{N} \cdot [\text{CH}_2]_3 \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$, which crystallises from benzene, melts at 127–128° (corr.), and when

treated successively with ammonia and hydrochloric acid is converted into *αδ-diaminovaleric acid*.

The dibenzoyl derivative of *αδ-diaminovaleric acid* is identical with ornithuric acid, and can be partially hydrolysed to the monobenzoyl derivative, which is identical with that obtained by Jaffé (Abstr., 1878, 585) from ornithuric acid. *αδ-Diaminovaleric acid* is probably the optically inactive form of ornithin. R. H. P.

Esters of Amino-acids. By EMIL FISCHER (*Sitzungsber. Akad. Wiss. Berlin*, 1900, 48, 1062—1083; *Ber.*, 1901, 34, 433—454).—The esters of the amino-acids are best prepared from the hydrochlorides by treatment with concentrated aqueous alkalis, hydrolysis is avoided at a low temperature, and when the solution has been saturated with potassium carbonate, the esters can be completely extracted with ether. With the exception of the crystalline derivatives of tyrosine, these esters are liquids, which have an alkaline reaction and can be distilled under reduced pressure; the solubility in water decreases with increasing molecular weight, the derivatives of aspartic and glutamic acids being, however, very soluble; the boiling points often lie wide apart, and the esters can be separated by fractional distillation, thus the isolation of the amino-acids from complicated mixtures, such as are obtained, for instance, by the hydrolytic decomposition of proteids, can be effected by the fractional distillation of the esters; they are easily hydrolysed by boiling with water or barium hydroxide, are characterised by their picrates, and easily form derivatives when treated with acid anhydrides, acid chlorides, halogen alkyls, carbimides, thiocarbimides, aldehydes, ketones, or carbonyl chloride; when heated with alcohol they are converted into compounds analogous to glycine anhydride.

The ethyl ester of glycine forms a *picrate* which crystallises in quadratic prisms and melts at 157° (corr.); it condenses with ethyl acetoacetate to form *diethyl acetoaceticglycine*, $\text{CO}_2\text{Et} \cdot \text{CH} : \text{CMe} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, which crystallises in clusters of colourless, long needles and melts at 53°, with acetylacetone to form *ethyl acetylacetoneglycine*,



which is obtained as a crystalline mass melting at 68° (corr.), with acetonylacetone to form a yellow oil, which turns a pine splinter, moistened with hydrochloric acid, a deep red colour, and when treated with alkalis yields 2 : 5-dimethylpyrrole-1-acetic acid, which crystallises in needles, melts at 130—131°, and decomposes in contact with moist air. Glycine ethyl ester, when treated with phenylthiocarbimide, yields *ethyl phenylthiocarbiminoacetate*, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, which crystallises in rhombic plates, melts at 85°, and gives a red solution with alkalis; when treated with phosgene, it yields *diethyl carbamidodiacetate*, $\text{CO}(\text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et})_2$, which crystallises in long, slender prisms and melts at 146° (corr.).

Alanine ethyl ester boils at 48° under 11 mm. pressure, has a sp. gr. 0.9846 at 12.5°, and forms a *picrate* which crystallises in yellow needles, and melts at 171° (corr.); when kept for some weeks, it is converted into the corresponding lactimide (3 : 6-dimethyl-2 : 5-diketopiperazine).

The *hydrochloride* of ethyl *α*-aminobutyrate, obtained by passing hydrogen chloride into an alcoholic solution of *α*-aminobutyric acid,

crystallises in needles, and can be readily converted into the free *ester*, which boils at 61.5° under 11 mm. pressure, has a sp. gr. 0.9655 at 12.5° , and forms a *picrate* which crystallises in slender prisms and melts at 127° (corr.); *ethyl β -aminobutyrate* boils at $59-60^{\circ}$ under 12.5 mm. pressure; attempts to esterify γ -aminobutyric acid resulted in the formation of its anhydride, the pyrrolidone, which boiled at 153° under 12 mm. pressure; 3:6-diethyl-2:5-diketopiperazine, $C_8H_{14}O_2N_2Et_2$, obtained by heating ethyl α -aminobutyrate at 170° , crystallises in lustrous leaflets and melts at 265° (corr.).

i-Ethyl leucine boils at 83.5° under 12 mm. pressure, has a sp. gr. 0.929 at 17° , forms a *picrate* which crystallises in yellow needles and melts at 136° (corr.), and a *d-tartrate*, which crystallises in lustrous leaflets and melts at 145° (corr.); the *l-ethyl ester* has a rotation $[\alpha]_D +13.1^{\circ}$ at 20° , is not racemised when hydrolysed, and forms a *picrate* which crystallises in small needles and melts at 129.5° (corr.). By means of this ester, pure *l-leucine* can be isolated from the products of the hydrolysis of horn; *leucinimide* (3:6-diisobutyl-2:5-diketopiperazine) crystallises from alcohol and melts at 271° (corr.); the *benzenesulphonic* derivative of *d-leucine* crystallises in clusters of needles, melts at $119-120^{\circ}$ (corr.), and has $[\alpha]_D -39^{\circ}$ at 20° (compare Abstr., 1900, i, 647), *i-acetyl leucine* crystallises in needles and melts at 161° (corr.).

i-Ethyl α -amino-n-caproate boils at $90-91^{\circ}$ under 11 mm. pressure, has a sp. gr. 0.9335 at 17° , forms a *picrate* which crystallises in prisms melting at 124° (corr.), and, when heated, yields 3:6-dibutyl-2:5-diketopiperazine, which crystallises in lustrous leaflets and melts at 268° (corr.). *i-Phenyl- α -alanine ethyl ester* is a viscous oil which has a sp. gr. 1.065 at 15° , and boils at 143° under 20 mm. pressure; it forms a *picrate* which crystallises in flat prisms melting at 156.5° (corr.), and when heated at 180° for 24 hours yields the phenyllactimide.

l-Tyrosine ethyl ester crystallises in flat prisms, melts at $108-109^{\circ}$ (corr.) has $[\alpha]_D +20.4^{\circ}$ at 20° , and, when heated at 180° for 24 hours is converted into a piperazine derivative. *Sarcosine ethyl ether* boils at 43° under 10 mm. pressure, has a sp. gr. 0.971 at 15.5° , and forms a *picrate* which crystallises in needles and melts at 149° (corr.). *l-Diethyl aspartate* is a viscous oil which boils at 126.5° under 11 mm. pressure, has a sp. gr. 1.089 at 17° and $[\alpha]_D -9.46^{\circ}$ at 20° . *d-Diethyl glutamate* boils at $139-140^{\circ}$ under 10 mm. pressure, has a sp. gr. 1.0737 at 17° and $[\alpha]_D +7.34^{\circ}$ at 20° .
R. H. P.

Canarin and ψ -Thiocyanogen. By ALWIN GOLDBERG (*J. pr. Chem.*, 1901, [ii], 63, 41-48).—Canarin obtained from thiocyanates, and the ψ -thiocyanogen products prepared by various chemical methods, are quite distinct substances. The author has determined the quantity of each produced from potassium thiocyanate by treatment with chlorine, bromine, fuming nitric acid, or potassium chlorate and hydrochloric acid, and from ammonium thiocyanate by interaction with ammonium persulphate.

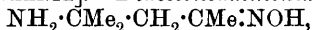
Canarin is separated from the ψ -thiocyanogen products as the slightly soluble sodium salt; on the addition of hydrochloric acid to a solution of this salt, canarin, $(C_8H_6ON_8S_7)_x$, is obtained as a light brown precipitate which, when dry, forms a yellowish-red powder. It is

extremely stable towards reducing agents; of its decomposition products obtained under various circumstances, cyanuric acid and its derivatives may be mentioned. In the formation of alkali salts, one-third of its hydrogen is replaced by the alkali metals.

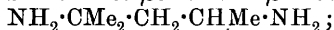
By the action of a dry halogen on a dry thiocyanate, and the treatment of the resulting thiocyanogen, $(\text{CNS})_x$, with alkali hydroxide, canarin is obtained in a yield of 30–40 per cent. of the thiocyanate employed. After the separation of the canarin sodium derivative, the residual alkaline solution yields, on addition of hydrochloric acid, a yellow, amorphous substance, $\text{C}_3\text{H}_4\text{ON}_4\text{S}_2$, in a quantity of about one-third to one-half of the dye produced in the same reaction; the filtrate contains sulphuric acid, hydrocyanic acid, and ammonia. When the substance, $\text{C}_3\text{H}_4\text{ON}_4\text{S}_2$, is heated with hydrochloric acid under pressure, it yields cyanuric acid; on treatment with ammonium sulphide under pressure, it furnishes dithiomelanurenic acid, and with ammonia under pressure, thioammeline. E. G.

Preparation of Doubly Unsaturated Hydrocarbons. By CARL HARRIES (*Ber.*, 1901, 34, 300–304).—When the phosphates of certain diamines are distilled, ammonia, ammonium pyrophosphate and an unsaturated hydrocarbon containing two double bonds are formed. The hydrochloride and sulphate of the diamine are less suited for this purpose.

[With SUREN ADAMIANTZ].—*Diacetoneaminoxime*,



is obtained from diacetoneamine, hydroxylamine hydrochloride, and potassium carbonate (compare Abstr., 1896, i, 318); it melts at 55–56°, and boils at 129–131° under 14 mm. pressure. It is reduced by sodium and alcohol to $\beta\delta$ -diamino- β -methylpentane,



this boils at 36–41° under about 12 mm. pressure, and forms a phosphate which melts at 187–188°. When the phosphate is distilled, methylisoprene (*methylpentadiene*), C_6H_{10} , perhaps $\text{C}_2\text{H} : \text{CMe} \cdot \text{CH} : \text{CHMe}$, is formed; it boils at 75–77° under 779 mm. pressure, and has sp. gr. 0.71761 at 16°.

[With ERNEST ATKINSON].—*Methylcyclohexenonehydroxylamino-oxime*,

$\text{OH} \cdot \text{NH} \cdot \text{CMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{C}(\text{NOH}) \\ \text{CH}_2 \text{---} \text{CH}_2 \end{smallmatrix} \text{CH}_2 \cdot \text{H}_2\text{O}$ (Abstr., 1898, i, 402), is reduced by sodium and alcohol to a diamine, $\text{C}_7\text{H}_{16}\text{N}_2$, which boils at 85–89° under 17 mm. pressure, and forms a sulphate, with $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, which was analysed. When the phosphate of the diamine is distilled, a dihydrotoluene (*methylcyclohexadiene*), C_7H_{10} , is obtained; this boils at 107–108° under 779 mm. pressure. C. F. B.

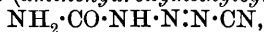
Hydouracil. By JULIUS TAFEL (*Ber.*, 1901, 34, 144).—The substance recently described by the author and Weinschenk (this vol., i, 72) as hydouracil has been previously described by Weidel and Roithner (Abstr., 1896, i, 470) as β -lactylcarbamide. A. H.

So-called Diazoguanidine. By ARTHUR HANTZSCH and A. VAGT (*Annalen*, 1901, 314, 339–369).—In many respects, the behaviour of diazoguanidine (Thiele, Abstr., 1892, 1298) is inconsistent with that of a true diazo-compound. The authors' investigation shows that

the salts of diazoguanidine, originally represented by the formula $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{N}:\text{N}\cdot\text{X}$, are actually derivatives of *carbaminoimino-azoimide*, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{N} < \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}$, and brings out the analogy between this compound and carbaminoazoimide (Thiele and Stange, Abstr., 1895, i, 252).

Carbaminoiminoazoimide nitrate is acid towards litmus, the aqueous solution, when boiled, yielding nitric acid and aminotetrazole, $\begin{smallmatrix} \text{N}-\text{N} \\ \text{N}\cdot\text{NH} \end{smallmatrix} > \text{C}\cdot\text{NH}_2$; the *nitrate* of the last-named substance crystallises from alcohol and melts at $174-175^\circ$, when it decomposes. Carbaminoiminoazoimide *hydrogen sulphate*, obtained by adding concentrated sulphuric acid to an alcoholic solution of the nitrate, behaves in a similar manner, yielding aminotetrazole and sulphuric acid; when heated with dilute sulphuric acid, the same change is brought about, 20 per cent. of azoimide also being produced. When the nitrate is reduced with cold stannous chloride, nitrogen is the main product, whilst hydrogen sulphide gives rise to nitrogen and guanidine.

Carbaminoazocyanide (aminohydroxymethylcyanotriazen),



obtained from carbaminoazoimide and hydrogen cyanide, is a brownish-yellow powder which darkens at 250° , and decomposes completely at higher temperatures; it is insoluble in water and all organic solvents, but forms alkali derivatives from which it may be regenerated by dilute acids.

Thiele observed that carbaminoiminoazoimide nitrate is resolved by sodium hydroxide (2 mols.) into cyanamideazoimide. The authors have succeeded in showing that carbaminoiminoazoimide is first formed from the action of the alkali (1 mol.); it exists unquestionably in the aqueous solution, but on evaporating the liquid, aminotetrazole is produced. When a cold aqueous solution of carbaminoiminoazoimide is treated with sodium hydroxide (2 mols.), cyanic acid and azoimide are produced, and conversely, carbaminoiminoazoimide may be synthesised from the two substances last named; similarly, aminotetrazole, which sodium hydroxide converts into cyanamide and azoimide, is produced when these compounds are brought together.

as-Dibenzylcyanamide, $\text{CN}\cdot\text{N}(\text{CH}_2\text{Ph})_2$, prepared from cyanamide and benzyl iodide at 50° , crystallises from ether in lustrous, white leaflets, and melts at $53-54^\circ$; it is identical with Wallach's cyanodibenzylamine (Abstr., 1899, i, 659). M. O. F.

Remarks on the Relation of Inorganic to Organic Chemistry. By AUGUST MICHAELIS (*Annalen*, 1901, 314, 276—280).—The author discusses the development and future of that branch of chemistry which deals with organic compounds containing such elements as phosphorus, arsenic, boron, silicon, sulphur, selenium, and tellurium. M. O. F.

Direct Hydrogenations Effected in the Presence of Reduced Nickel: Preparation of Hexahydrobenzene. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1901, 132, 210—212. Compare Abstr., 1897, i, 305, 545; 1899, i, 555).—When hydrogen, saturated

at the ordinary temperature with the vapour of benzene, is led over finely divided nickel at 180—200°, combination of the two gaseous reagents takes place, resulting in the formation of *cyclohexane*. The liquid product is quite free from benzene and its partially hydrogenated derivatives. When the hydrocarbon is in excess the product consists of *cyclohexane* and unaltered benzene. At 300°, the *cyclohexane* is decomposed while still in contact with the nickel, and yields methane and a deposit of carbon. In all probability, the first stage of this reaction consists in the decomposition of 1 mol. of the *cyclohexane* into 3 mols. of ethylene, the gaseous hydrocarbon being then broken up into methane and carbon (compare Abstr., 1897, i, 305, 545). The higher homologues of benzene also undergo hydrogenation in a similar manner, whilst nitrobenzene is easily reduced to aniline.

G. T. M.

Constitution of Benzene. By GEORGE M. RICHARDSON (*Amer. Chem. J.*, 1901, 25, 123—144).—The author draws attention to a number of properties in which ortho- and para-derivatives of benzene resemble one another, but in which they differ from isomeric meta-compounds. Among the points dealt with are (1) Phenomena of substitution; (2) influence of substituents on the properties of a compound; (3) phenomena of reduction and oxidation. The conclusion drawn is that Claus' diagonal formula best represents the structure of the benzene molecule.

J. J. S.

Formation and Preparation of Propylbenzene. By F. BOURROUX (*Compt. rend.*, 1901, 132, 155—157).—The hydrocarbons, α -diphenylpropane, and propylbenzene, are produced by heating at 60° a mixture of benzene, aluminium chloride, and trimethylene dibromide. The propylbenzene, on treatment with bromine and aluminium bromide, yields pentabromopropylbenzene and a small quantity of hexabromobenzene; the latter substance is produced from *isopropylbenzene*, and the quantity obtained shows that the crude hydrocarbon consists chiefly of *n*-propylbenzene with 1·3 per cent. of cumene. The hydrocarbon produced from benzene and propylene dibromide in the presence of aluminium chloride consists almost wholly of the normal isomeride, only a trace of hexabromobenzene being obtained on bromination. The hydrocarbon derived from $\alpha\beta$ -diphenylpropane by distilling this substance from powdered aluminium chloride yields equivalent proportions of pentabromopropylbenzene and hexabromobenzene, and therefore consists of equal quantities of *n*-propylbenzene and cumene.

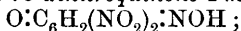
G. T. M.

Tetranitrobenzene, Nitrodinitrosobenzene, and Trinitrophenylhydroxylamine. By RUDOLF NIETZKI and RICHARD DIETSCHY (*Ber.*, 1901, 34, 55—60).—By the action of picryl chloride on hydroxylamine hydrochloride in presence of sodium acetate, a *dinitrodinitrosobenzene* is produced, to which the formula $C_6H_2(NO_2)_2 \begin{smallmatrix} N \cdot O \\ \llcorner \\ N \cdot O \end{smallmatrix}$ [(NO₂)₂ : (NO)₂ = 1 : 3 : 4 : 5] is assigned; it separates in glistening,

golden flakes, melts at 133° , dissolves readily in hot water, alcohol, ether, or acetic acid, and is perhaps the same substance which Michael and Brown (Abstr., 1887, 663) described as dipicrylhydroxylamine. Like dinitrosobenzene, it is relatively very stable, but is oxidised by nitric acid of sp. gr. 1.52 to 1:2:3:5-tetranitrobenzene, $C_6H_2(NO_2)_4$, which crystallises from alcohol in minute, yellow needles, melts at 116° , is reduced by stannous chloride and hydrochloric acid to tetraaminobenzene, and with aniline forms an additive product crystallising from alcohol in red needles and melting at 180° .

2:4:6-Trinitrophenyl-1-hydroxylamine, $C_6H_2(NO_2)_3 \cdot NH \cdot OH$, formed by the action of picryl chloride on hydroxylamine hydrochloride when no sodium acetate is used, crystallises from alcohol, in which it is only slightly soluble, in minute, yellow needles, melts at 174° , and differs entirely from the substance melting at $99-100^{\circ}$ which Michael and Brown prepared by the action of hydroxylamine on ethyl picrate, and described as picrylhydroxylamine; it forms an additive product with aniline, is reduced by stannous chloride and hydrochloric acid to tetraaminobenzene, and by ammonium sulphide to dinitrodiaminobenzene, and is oxidised by nitric acid to tetranitrobenzene. Alcoholic potassium hydroxide converts the hydroxylamine into isopicric acid, $C_6H_3O_7N_3$, which crystallises from water or alcohol in dark yellow needles and melts at $117-118^{\circ}$ (picric acid melts at 122°); the potassium salt crystallises in brown flakes with a violet lustre, and is three times as soluble in water as potassium picrate; the structure of the acid has not been determined, but it is suggested that one of the nitro-groups has been replaced by hydroxyl, and the hydroxylamine group oxidised to a nitro-group.

1:3:5-Trinitro-2-nitrosobenzene, $C_6H_2(NO_2)_3 \cdot NO$, prepared by oxidising the hydroxylamine with chromic acid in acetic acid solution, crystallises from acetic acid in greenish-yellow flakes, melts at 198° , and shows a normal molecular weight when dissolved in boiling benzene. Nitric acid of sp. gr. 1.52 does not oxidise it to tetranitrobenzene, but converts it into a substance, $C_6H_3O_6N_3$, having the composition of a trinitrobenzene, but which is regarded as 3:5-dinitro-4-nitrosophenol, $NO \cdot C_6H_2(NO_2)_3 \cdot OH$, or 3:5-dinitroquinone-4-monoxime,

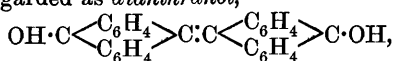


it crystallises from alcohol in yellow needles, melts at 110° , dissolves in alkali carbonates, and is reprecipitated by acids. T. M. L.

Action of Nitric Acid on Anthracene. By OTTO DIMROTH (Ber., 1901, 34, 219—223. Compare Meisenheimer, this vol., i, 135).—Nitroanthracene can be obtained, not only from the products, $C_{14}H_{10}$, HNO_3 and $C_{14}H_{10}$, $2NO_2$, obtained by Liebermann and Lindemann by the action of nitrous fumes on anthracene (Abstr., 1881, 99), and the compound, $C_{14}H_{10}$, $EtNO_3$, prepared by the action of nitric acid and alcohol on anthracene (A. G. Perkin, Trans., 1891, 59, 637), but also by the action of alkalis on the nitroacetate and nitrochloride.

Anthracene nitroacetate, $NO_2 \cdot CH < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > CH \cdot OAc$, prepared by the action of 1 mol. of nitric acid on anthracene suspended in glacial acetic acid, is a yellow substance which has not been crystallised, but is

converted by warm dilute sodium hydroxide into nitroanthracene. The *nitrochloride*, $\text{NO}_2 \cdot \text{CH} \langle \text{C}_6\text{H}_4 \rangle \text{CHCl}$, prepared by adding strong hydrochloric acid to the nitration mixture, crystallises from benzene in broad, colourless needles, melts at about 163° , and is readily converted into nitroanthracene, the yield of which exceeds slightly the weight of anthracene used. Nitroanthracene is also produced when sulphuric acid is added to the nitration mixture, but without this addition the mixture slowly decomposes, giving, at first, a *substance* which separates in stout, white crystals, dissolves in dilute sodium hydroxide with an intense red coloration, crystallises from benzene in white needles, and melts at 135° ; anthraquinone subsequently separates. When heated on the water-bath, a substance, $\text{C}_{28}\text{H}_{18}\text{O}_2$, is produced which is regarded as *dianthranol*,



or, more probably, *dianthrone*, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{CH} \langle \text{C}_6\text{H}_4 \rangle \text{CO}$; this is identical with the product obtained by Orndorff and Bliss (Abstr., 1896, i, 570) from anthranol, and described by them as a polymeride, $\text{C}_{28}\text{H}_{20}\text{O}_2$; the fact that it is an oxidation product is shown by its formation from anthranol by treatment with ferric chloride, a reaction analogous to the formation of α - and β -dinaphthols from α - and β -naphthols.

T. M. L.

Triphenylchloromethane. By JAMES F. NORRIS and WARREN W. SANDERS (*Amer. Chem. J.*, 1901, 25, 54—62. Compare Gomberg, Abstr., 1901, i, 77).—The authors have obtained a nearly theoretical yield of triphenylchloromethane by a method differing somewhat from that recently described by Gomberg; they have also isolated a brown, crystalline intermediate *product*, $\text{Al}_2\text{Cl}_3 \cdot 2\text{CPh}_3\text{Cl}$, which decomposes rapidly in the air, and when heated begins to decompose at 122 — 125° .

E. G.

Non-existence of Tervalent Carbon. By JAMES F. NORRIS (*Amer. Chem. J.*, 1901, 25, 117—122. Compare Gomberg, this vol., i, 77).—The reaction of zinc on triphenylchloromethane is much more rapid in ethyl acetate than in benzene solution; in the former case, hydrogen is evolved and the action completed within 2—3 minutes, whereas in benzene solution the action goes on for 5—6 days and no hydrogen is evolved. The product obtained by either method when brought into contact with air yields Gomberg's peroxide. The authors conclude that Gomberg's unsaturated hydrocarbon, triphenylmethyl (*loc. cit.*), is really *diphenylphenylenemethane*, $\text{CPh}_2 : \text{C}_6\text{H}_4$, and is obtained by the elimination of hydrogen chloride from the chloro-derivative. Gomberg's peroxide is only formed when moist air acts on the hydrocarbon, and is hence probably due to the combined action of moisture and oxygen. The action of iodine on the hydrocarbon, if the author's view of its constitution be accepted, must be due to the intermediate formation of hydrogen iodide. In many properties, diphenylphenylene-methane resembles tetrahydronaphthalene.

J. J. S.

Crotonic and *iso*Crotonic Acids. By WILHELM AUTENRIETH and PAUL SPIESS (*Ber.*, 1901, **34**, 189—197).—On boiling crotonic acid with acetic anhydride, a mixture of acetic crotonic anhydride and crotonic anhydride is apparently obtained (compare this vol., i, 185), which, without further purification, yields with aniline the *anilide* $\text{H}\cdot\overset{\text{Br}}{\underset{\text{H}\cdot\text{C}\cdot\text{CO}\cdot\text{NHPh}}{\overset{\text{H}\cdot\text{C}\cdot\text{Me}}{\text{C}}}}$; this crystallises from water in colourless, lustrous needles or thick prisms, melts at 115° , dissolves in 2000 parts of water at 15° , and can also be obtained by the action of aniline on crotonyl chloride, formed by the action of phosphorus pentachloride on crotonic acid. With bromine, the anilide yields $\alpha\beta$ -*dibromobutyryl*-

anilide, $\text{H}\cdot\overset{\text{Br}}{\underset{\text{H}\cdot\text{C}\cdot\text{CO}\cdot\text{NHPh}}{\overset{\text{H}\cdot\text{C}\cdot\text{Me}}{\text{C}}}}$, which crystallises from dilute alcohol in lustrous plates, melts at 159° , and is also formed from Kolbe's $\alpha\beta$ -*dibromobutyric acid* (*J. pr. Chem.*, 1842, **25**, 385) by the successive action of phosphorus pentachloride and aniline.

isocrotonylanilide, $\text{H}\cdot\overset{\text{Me}\cdot\text{C}\cdot\text{H}}{\underset{\text{H}\cdot\text{C}\cdot\text{CO}\cdot\text{NHPh}}{\overset{\text{Br}}{\text{C}}}}$, is formed by the action of aniline on the mixed anhydrides obtained by boiling acetic anhydride with *isocrotonic acid*; it crystallises from water at 60° in slender, silky needles, melts at 73 — 74° , and is soluble in 1100 parts of water at the ordinary temperature. When *isocrotonic acid* is treated with phosphorus pentachloride at the ordinary temperature, and then with aniline, it yields, not *isocrotonylanilide*, but the isomeric *crotonylanilide*, owing to the *isocrotonyl chloride* being transformed into *crotonyl chloride*; if, however, during the formation of the chloride, the mixture is cooled, no such change occurs, and *isocrotonylanilide* is ultimately obtained. The latter is completely transformed into *crotonylanilide* when heated for 8 hours at 180 — 200° , and is thus the labile form of

the *anilide*. *iso- $\alpha\beta$ -Dibromobutyrylanilide*, $\text{H}\cdot\overset{\text{Me}\cdot\text{C}\cdot\text{H}}{\underset{\text{H}\cdot\text{C}\cdot\text{CO}\cdot\text{NHPh}}{\overset{\text{Br}}{\text{C}}}}$, obtained

from it by the addition of bromine, melts at 115° , and is more soluble in alcohol than its isomeride; it is also formed by the successive treatment of *iso- $\alpha\beta$ -dibromobutyric acid* with phosphorus pentachloride and aniline. These facts establish the correctness of Wislicenus' views (*Abstr.*, 1889, 236) as to the existence of two different *dibromobutyric acids*.

With acetic anhydride, both β -*chlorocrotonic acid* and β -*chloroisocrotonic acid* yield the corresponding anhydrides, which interact normally with aniline and phenylhydrazine; it is noteworthy that the former acid is not converted by this treatment into the *iso-acid*, although rapidly transformed by phosphorus pentachloride into *isocrotonyl chloride* (*Abstr.*, 1896, i, 591). β -*Chloroisocrotonylanilide*, $\text{H}\cdot\overset{\text{Me}\cdot\text{C}\cdot\text{Cl}}{\underset{\text{H}\cdot\text{C}\cdot\text{CO}\cdot\text{NHPh}}{\overset{\text{Br}}{\text{C}}}}$, crystallises from dilute alcohol in slender prisms

melting at 108° , and the *phenylhydrazide* from benzene on adding light petroleum in lustrous leaflets melting at 114° . β -*Chlorocrotonyl*-

anilide, $\text{Cl}\cdot\text{C}\cdot\text{Me}$
 $\text{H}\cdot\text{C}\cdot\text{CO}\cdot\text{NHPh}$, forms slender needles melting at 122—123°, and the *phenylhydrazide* flat needles melting at 130°. W. A. D.

Synthesis of Amines by the Aid of Alkyl Salicylates. By ALFRED TINGLE (*Amer. Chem. J.*, 1901, 25, 144—155. Compare Abstr., 1900, i, 544 and 641).—It has previously been shown that secondary amines are obtained by the action of alkyl salicylates on aniline. Ammonia acts on methyl salicylate at its boiling point, yielding dimethylaniline and salicylamide, the latter being then partly converted into polysalicylonitrile; the reaction between ammonia and ethyl or *iso*amyl salicylate is so slow that the products could not be investigated. Benzanilide is the only product obtained by the action of aniline on methyl benzoate, whether the former is in excess or not. Benzoic acid and dimethylaniline give a small amount of methyl benzoate and a tarry substance. It is probable that the action between an aromatic ester and aniline is a reversible one, $\text{R}\cdot\text{CO}_2\text{R}' + \text{NH}_2\text{Ph} \rightleftharpoons \text{R}\cdot\text{CO}_2\text{H} + \text{NHPhR}'$, but that in the case of salicylates the reaction becomes no longer reversible owing to the fact that the salicylic acid is decomposed into phenol and carbon dioxide as fast as it is formed.

When methyl salicylate (2 mols.) and aniline (1 mol.) are boiled for 6 hours, the product is dimethylaniline, and not methylaniline, the product formed when aniline is in excess.

Methyl *p*-hydroxybenzoate (1 mol.) and aniline (3 mols.), when boiled for 4 hours, give dimethylaniline and phenol in addition to the unchanged substances. Methyl *m*-hydroxybenzoate crystallises from a mixture of benzene and light petroleum in colourless needles melting at 70°. When boiled with excess of aniline, it is partly converted into *m*-hydroxybenzanilide, but no secondary or tertiary base is formed, no doubt owing to the fact that the acid, unlike the ortho- and para-acids, is stable. J. J. S.

Dimethylaniline Oxide. By EUGEN BAMBERGER and PAUL LEYDEN (*Ber.*, 1901, 34, 12—26. Compare Bamberger and Tschirner, Abstr., 1899, i, 347 and 682).—In preparing dimethylaniline oxide, the yield is improved by using hydrogen peroxide previously neutralised with magnesia. Small quantities of nitrobenzene are formed, apparently owing to the following changes, $\text{NPhMe}_2 \rightarrow \text{NHPhMe} \rightarrow \text{PhNO} \rightarrow \text{Ph}\cdot\text{NO}_2$.

When dry dimethylaniline oxide hydrochloride is heated in a stream of carbon dioxide for 150 hours at 75—80°, it yields 26 per cent. of its weight of a mixture of dimethylaniline and methylaniline in the proportion 3:2, along with traces of aniline and *o*-dimethylaminophenol, 6 per cent. of a mixture of tetramethyl-*pp*-diaminodiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}\cdot\text{NMe}_2)_2$, and bisdimethylaniline (Lippmann and Lange, Abstr., 1881, 161), and about 8 per cent. of mixed *p*-dimethylaminophenol (von Pechmann, *Ber.*, 1899, 32, 3682, note) and *p*-aminophenol; 18 per cent. of a violet amorphous powder is also formed along with 10 per cent. of resin and about 2 per cent. of a crystalline, slightly acid substance melting at 157°, which was not analysed.

When the hydrochloride is boiled for 70 hours with dilute hydrochloric acid, it yields principally dimethylaniline with only traces of methylaniline and aniline; formic acid, quinol, tetramethylbenzidine, $C_{12}H_8(NMe_2)_2$, bisdimethylaniline, dimethyl-*p*-aminophenol, and traces of *p*-aminophenol are also formed along with a crystalline substance melting at 135° and having the properties of an aminophenol.

Dry dimethylaniline oxide, on being heated for 10 minutes at 140 – 150° , yields formaldehyde in quantity, along with dimethylaniline and methylaniline in the proportion 3 : 2, and traces of tetramethyldiaminodiphenylmethane and dimethylamino-*o*-phenol. When the oxide is heated with concentrated sulphuric acid for 12 hours at 65 – 75° , it suffers isomeric change to the extent of 60 per cent. into a mixture of equal parts of *o*- and *p*-dimethylaminophenol; the anhydride $(C_6H_4 \cdot NMe_2)_2O$ of the former (Holzmann, Abstr., 1888, 1080) is also obtained, along with dimethylaniline and methylaniline, in the proportion 9 : 1.

The production of methylaniline probably takes place thus: $NPhMe_2 \cdot O = NHMePh + CH_2O$, the formaldehyde then interacting with dimethylaniline to form tetramethyldiaminodiphenylmethane. Aniline is formed similarly along with formaldehyde owing to oxidation of the methylaniline by oxygen derived from the dimethylaniline oxide; the dimethylaminophenols, formed from the latter by isomeric change, yield methylaminophenol and aminophenol in the same way. Quinol is formed by the hydrolysis of dimethyl-*p*-aminophenol. W. A. D.

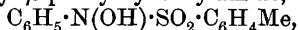
Action of Nitric Acid on the Esters of Phenylmethylamino-formic Acid. By PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 451–453).—*Methyl phenylmethylcarbamate*, obtained by the action of methylaniline on methyl chloroformate, is a crystalline substance, which melts at 44° and boils at 243° ; when treated with a mixture of sulphuric and nitric acids, it yields the 2 : 4-dinitro-derivative, which crystallises in glossy, transparent crystals and melts at 98° ; the corresponding dinitro derivative of the ethyl ester melts at 112° . Both dinitro-derivatives, when heated in sealed tubes at 150° with fuming hydrochloric acid, decompose, giving carbon dioxide, alkyl chlorides, and 2 : 4-dinitromethylaniline. The corresponding 2 : 4 : 6-trinitro-compounds were obtained by the action of methyl iodide on the silver salts of the 2 : 4 : 6-trinitrophenylcarbamic esters; the *methyl* ester is a yellow, crystalline substance and melts at 112 – 113° , the *ethyl* ester melts at 65° . R. H. P.

Action of Toluene-*p*-sulphinic Acid on Nitrosobenzene. By EUGEN BAMBERGER and ADOLF RISING (*Ber.*, 1901, 34, 228–241).—The following substances have been obtained by the action of toluene-*p*-sulphinic acid on nitrosobenzene dissolved in alcohol, acetic acid, or chloroform: (1) *p*-Aminophenol. (2) Aniline.

(3) *p*-Aminophenol toluene-*p*-sulphonate, $OH \cdot C_6H_4 \cdot NH_2, C_6H_4Me \cdot SO_3H$, which can also be prepared from *p*-aminophenol and toluene-*p*-sulphonic acid; it forms glistening, silvery-white flakes, melts and decomposes to a violet oil at 245° , dissolves readily in water and alcohol, less readily in other solvents, and yields *p*-aminophenol when acted on by sodium hydroxide.

(4) *p*-Aminophenyl toluene-*p*-sulphonate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, was obtained as its toluene-*p*-sulphonate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{C}_7\text{H}_7\cdot\text{SO}_3\text{H}$, in the form of white needles melting at $242.5\text{--}243^\circ$ to a violet liquid; the ester itself crystallises from alcohol in long, glassy prisms, forms a crystalline hydrochloride, oxalate, and sulphate, is hydrolysed only with great difficulty to *p*-aminophenol and toluenesulphonic acid, has also been prepared synthetically by reducing the corresponding nitro-ester, and is probably formed by isomeric change from an unstable additive product, $\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, of nitrosobenzene, and the sulphinic acid. The monoacetyl derivative, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, crystallises from benzene in flat, white, glistening needles and melts at $145.5\text{--}146^\circ$; the diacetyl derivative, $\text{NAc}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, crystallises from alcohol, melts at 101° , and is converted into the preceding compound by hot aqueous sodium hydroxide. When diazotised, the ester condenses with β -naphthol to form a compound, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, which crystallises in glistening, orange-red needles, and melts at $157\text{--}157.5^\circ$.

(5) β -Tolylsulphonyl- β -phenylhydroxylamine,



a stable additive product of nitrosobenzene and the sulphinic acid, forms white, glistening plates, melts at $143\text{--}143.5^\circ$, and is identical with the substance prepared by Bretschneider (Abstr., 1897, i, 421) from β -phenylhydroxylamine and toluene-*p*-sulphinic acid, and with the synthetical product prepared from β -phenylhydroxylamine and toluenesulphonic chloride.

(6) *pp*-Toluenedisulphoxide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{S}\cdot\text{C}_6\text{H}_4\text{Me}$, which is only produced in small quantities, and is identical with the substance prepared by Otto and Gruber from toluenesulphinic acid and water.

(7) A neutral substance, which formed straw-yellow crystals, melted at $161\text{--}162^\circ$, and is probably an oxy-compound.

p-Nitrophenyl toluene-*p*-sulphonate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, prepared by the action of toluene-*p*-sulphonic chloride on sodium *p*-nitrophenoxide in alcoholic solution, forms square, glistening tablets, melts at $97\text{--}97.5^\circ$, and is reduced by stannous chloride and hydrochloric acid to the amino-ester already described. The *o*-nitro-ester forms compact, glassy prisms and melts at 81.5° ; the *o*-amino-ester forms hard, white, glassy needles and melts at $101\text{--}101.5^\circ$.

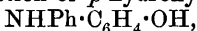
T. M. L.

Action of *p*-Tolylsulphinic Acid on β -Phenylhydroxylamine. By EUGEN BAMBERGER and ADOLF RISING (*Ber.*, 1901, 34, 241—253. Compare Bretschneider, Abstr., 1897, i, 421).—The products of the action of toluene-*p*-sulphinic acid on β -phenylhydroxylamine are similar to those obtained from nitrosobenzene, but include also *p*-aminophenyl-*p*-tolylsulphone; this is probably due to the conversion of the hydroxylamine into nitrosobenzene and aniline, the formation of azoxybenzene being prevented by the presence of the sulphinic acid.

p-Tolylaminophenylsulphone, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, forms silky, white needles, melts at 181.5° , and can be prepared synthetically by the action of phosphoric oxide on aniline hydrochloride and toluene-*p*-sulphonic acid; the acetyl derivative crystallises from alcohol in white needles, melts at 198° , and dissolves readily in acetone. T. M. L.

Isomerism of Thiocyanic Esters. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 57—58).—Phenyl thiocyanate, freshly prepared, gave the following results: Heat of combustion at const. vol. 7675·8 cal.; molecular heat of combustion at const. press. +1037·4 Cal.; heat of formation from elements, -63·7 Cal. The heat of formation of phenylthiocarbimide previously determined is -46·5 Cal., and hence the difference between the two isomerides is 17·2 Cal., which agrees with the difference between alkyl thiocyanates and alkylthiocarbimides. Determinations of the heat of combustion of the same specimen of phenyl thiocyanate at intervals show that in the course of a few weeks at summer temperature it changes to a large extent into phenylthiocarbimide. C. H. B.

Mechanism of the Change of Arylhydroxylamines into Aminophenols. II. By EUGEN BAMBERGER (*Ber.*, 1901, 34, 61—68. Compare this vol., i, 140).—In support of the view that the first product in the isomeric change of phenylhydroxylamines is an unsaturated substance, $C_6H_5 \cdot N:$, a number of reactions are quoted in which additive products are formed of the types $C_6H_5 \cdot NHX$ and $HX:C_6H_4:NH$, or $X \cdot C_6H_4 \cdot NH_2$. To the first type belong the formation of *o*- and *p*-aminodiphenylamine, $NHPh \cdot C_6H_4 \cdot NH_2$, by the action of aniline on phenylhydroxylamine, the formation of *p*-hydroxydiphenylamine,



in the action of dilute sulphuric acid on phenylhydroxylamine, the formation of *p*-hydroxyphenyl-*p*-tolylamine, $C_6H_4Me \cdot NH \cdot C_6H_4 \cdot OH$, by the action of phenol on *p*-tolylhydroxylamine, and the formation of a primary base, $C_{16}H_{20}ON_2$, probably $C_6H_3Me_2 \cdot NH \cdot O \cdot C_6H_2Me_2 \cdot NH_2$, in the action of dilute sulphuric acid on 2:6-dimethylphenylhydroxylamine. To the second type belong the formation of *p*-aminophenol-sulphonic acid in the action of sulphuric acid on phenylhydroxylamine, $N \cdot C_6H_5 \rightarrow NH:C_6H_5 \cdot O \cdot SO_3H \rightarrow NH_2 \cdot C_6H_3(OH) \cdot SO_3H$, the formation of *p*-hydroxy-*p*-aminodiphenyl, $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot OH$, by the action of phenol on phenylhydroxylamine, and of benzidine when aniline is used, the formation of di-*p*-diaminodiphenyl ether, $O(C_6H_4 \cdot NH_2)_2$, in the action of concentrated sulphuric acid on phenylhydroxylamine, and the formation of phenetidine by the action of alcoholic sulphuric acid on phenylhydroxylamine. Additional evidence of the existence of the type $C_6H_5 \cdot N:$ is afforded by the formation of polymeric benzyleneimine, $(CH_2:C_6H_4:NH)_n$, in the action of sulphuric acid on *p*-tolylhydroxylamine, and of aminophenylnitrotolylmethane, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3Me \cdot NO_2$, when *p*-nitrotoluene is also present. The products of the action of phenol on phenylhydroxylamine and *p*-tolylhydroxylamine belong to the first and second types respectively, showing that the *p*-methyl group favours the formation of compounds of the second type, as has already been pointed out in the case of the ψ -quinols (*loc. cit.*).

A similar explanation is given of the formation of *op*- and *pp*-dinitrodiphenylamine, $NH(C_6H_4 \cdot NO_2)_2$, by the spontaneous decomposition of a solution in benzene of phenylnitrosohydroxylamine, $C_6H_5 \cdot N(NO)OH$ (*Abstr.*, 1898, i, 366), namely, the formation of *p*-nitrosophenylhydroxylamine by isomeric change of the unsaturated substance, $NO \cdot C_6H_4 \cdot N:$ by subsequent loss of water, condensation with unchanged

nitrosoamine to $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{NO}) \cdot \text{OH}$, loss of HNO from the condensation product, and oxidation of the resulting dinitrosodiphenylamine to dinitrodiphenylamine; the formation of *p*-nitrodiphenylamine and its nitrosoamine would follow in a similar manner by the condensation of phenylnitrosohydroxylamine with the unsaturated substance from phenylhydroxylamine.

T. M. L.

Regularities in the Distillation of Dilute Aqueous Phenol Solutions. By ALEXANDER NAUMANN and WILHELM MÜLLER (*Ber.*, 1901, 34, 224—228).—Dilute solutions of phenol were distilled into a burette in such a way that quantities of 100 c.c. were successively collected, whilst the volume of the solution in the flask was kept constant at 500 c.c. by the gradual addition of water. It was found that the 100 c.c. of distillate always contained a constant proportion of the phenol in the flask, the mean value of the ratio being 0.335, whilst successive distillates contained proportions of phenol decreasing in a constant ratio the mean value of which was 0.665 ($= 1 - 0.335$). The distillation of the phenol proceeds, therefore, according to the laws of an infinite geometrical progression, the sum of which represents the whole weight of phenol taken for the distillation.

T. M. L.

Action of Sulphuric Acid on Phenetole. By WILLIAM B. SCHÖBER and HENRY L. BOWERS (*Amer. Chem. J.*, 1901, 25, 69—76).—When a mixture of concentrated sulphuric acid and phenetole is either left at the ordinary temperature or heated, *p*-phenetolesulphonic acid is obtained together with a small proportion of the *m*-acid, whereas according to Moody (*Proc.*, 1892, 8, 90, 214) only the former is produced.

By the action of fuming sulphuric acid on phenetole at 85° , a minute quantity of phenetoledisulphonic acid is formed.

E. G.

Quinols. By THEODOR ZINCKE (*Ber.*, 1901, 34, 253—257).—Bamberger, in his account of quinols [ψ -quinols] (this vol., i, 140) has overlooked the fact that the author has already prepared a member of this class of compounds, namely, the substance $\text{CO} \begin{smallmatrix} \text{CCl}:\text{CCl} \\ \text{CCl}:\text{CCl} \end{smallmatrix} \text{CMe} \cdot \text{OH}$ (*Abstr.*, 1896, i, 214). This is obtained by oxidising tetrachloro-*p*-cresol with boiling nitric acid of sp. gr. 1.35; in the cold a nitroketone is formed which, however, yields the ψ -quinol when heated with acetic acid; on reduction with zinc and hydrobromic acid, it is reconverted into the tetrachlorocresol; it dissolves in alkalis, forms an acetyl derivative, and reacts with alkalis and with aniline, exchanging one atom of chlorine for the groups OH or NHPH respectively, and forming products that are still quinone derivatives; it does not react with phenylhydrazine.

Tetrabromo-*p*-ethylphenol can also be converted into a ψ -quinol, $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \text{CEt} \cdot \text{OH}$, which melts at 140° , and its acetyl derivative at 124° ; when treated with cold concentrated sulphuric acid, it forms yellow tribromoethyl-*p*-quinone, $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CEt} \end{smallmatrix} \text{CO}$, which melts at

118—120°, and can be converted into a colourless *quinol* melting at 141°.

Tetrabromo-*p*-cresol yields a *ψ-quinol*, $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \text{CMe}\cdot\text{OH}$, melting at 205°; the *acetyl* derivative melts at 175—176°.

Tribromo-*m*-xylenol yields a *ψ-quinol*, $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CMe}:\text{CBr} \end{smallmatrix} \text{CMe}\cdot\text{OH}$, melting at 176°; the *acetyl* derivative melts at 129°. The acid character of this and of the last *ψ-quinol* is very feeble.

Tribromophenols are less readily oxidised to *ψ-quinols* by nitric acid of sp. gr. 1·4 in acetic acid solution; if the action is stopped after a short time, dibromonitrophenols are obtained. Tribromo-*p*-cresol yields a *ψ-quinol*, $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}=\text{CH} \end{smallmatrix} \text{CMe}\cdot\text{OH}$, which melts at 128°, its *acetyl* derivative melting at 127—128° (Abstr., 1900, i, 545). Tribromo-ethylphenol yields a *ψ-quinol*, $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}=\text{CH} \end{smallmatrix} \text{CEt}\cdot\text{OH}$, melting at 105°. Both these *ψ-quinols* are soluble in alkalis.

Monochloro- and monobromo-*p*-cresol are only attacked by nitric acid of sp. gr. 1·5, and the products are not *ψ-quinols* (Abstr., 1900, i, 545), but nitroquinones, $\text{CO} \begin{smallmatrix} \text{CCl}=\text{CMe} \\ \text{C}(\text{NO}_2)=\text{CH} \end{smallmatrix} \text{CO}$, &c. C. F. B.

Derivatives of Catechol. By OSCAR WISINGER (*Monatsh.*, 1900, 21, 1007—1020).—4-Nitrocatechol diethyl ether, obtained by the action of 75 per cent. nitric acid on catechol diethyl ether dissolved in glacial acetic acid, crystallises in bright yellow needles, melts at 73—75°, and, when reduced with tin and hydrochloric acid, yields the *hydrochloride* of the corresponding amino-compound; when boiled with acetic anhydride, this forms the *diacetyl* derivative, $\text{C}_6\text{H}_3(\text{OEt})_2\cdot\text{NAc}_2$, which crystallises in transparent leaflets, melts at 120—121°, and when partially hydrolysed yields the *monoacetyl* derivative, which crystallises in white leaflets melting at 125—126°. When catechol methyl ether is nitrated in a similar manner, a mixture of 1-methoxy-2-ethoxy-4-nitrobenzene and 1-ethoxy-2-methoxy-4-nitrobenzene is obtained; one of these is soluble in alcohol, crystallises in small, yellow needles, melts at 65—67°, and, when reduced, yields the *hydrochloride* of an amino-compound the *diacetyl* and *monoacetyl* derivatives of which melt respectively at 117—119° and 136—138°; the other is only slightly soluble in alcohol, crystallises in long, yellow needles, melts at 100—102°, and when reduced yields the *hydrochloride* of an amino-compound the *diacetyl* and *monoacetyl* derivatives of which melt respectively at 135—137° and 142—143°.

The constitution of these compounds was determined by their conversion into hydroxyquinol triethyl ether. R. H. P.

Alkyl Ethers of Phloroglucinols. II. Ethers of Methylphloroglucinol. By JOSEF HERZIG and FRANZ THEUER (*Monatsh.*, 1900, 21, 852—865. Compare Abstr., 1900, i, 545; and Reisch, Abstr., 1899, i, 803).—Methylphloroglucinol dimethyl ether is not altered by treatment with alcoholic potash, and when treated with

methyl iodide and sodium is converted into the *trimethyl ether*, which is a colourless, mobile oil boiling at 140—142° under 18 mm. pressure, and solidifying at -13° to a white, crystalline mass, which melts at 10—13°; the corresponding *methylphloroglucinol dimethyl ethyl ether* is obtained as a mass of silky crystals, melts at 38°, and boils at 149—151° under 16 mm. pressure; *dibromomethylphloroglucinol dimethyl ether*, $\text{OH}\cdot\text{C}_6\text{MeBr}_2(\text{OME})_2$, obtained by the action of bromine on the dimethyl ether dissolved in glacial acetic acid, crystallises in needles, melts at 73—74°, and can be recovered unaltered after treatment with alcoholic potash; the formation and behaviour of these compounds show that in methylphloroglucinol dimethyl ether the third hydroxyl group is "fixed" just as in the dialkyl ethers of phloroglucinol. Tetramethylphloroglucinol methyl ether, when treated with bromine, yields dibromotetramethylphloroglucinol, which, when boiled with acetic anhydride, is converted into *acetylbromotetramethylphloroglucinol*, $\text{C}_6\text{Me}_4\text{O}_2\text{Br}\cdot\text{OAc}$, which crystallises in lustrous needles and melts at 135°. The oil, probably hexamethylphloroglucinol, obtained along with tetramethylphloroglucinol by the methylation of methylphloroglucinol methyl ether, and described by Reisch (*loc. cit.*) as penta-methylphloroglucinol, when treated with bromine yields a compound which crystallises in the monoclinic system [$a:b:c=1.373:1:1.116$, $\alpha=85^\circ 10'$], melts at 129—131°, and is probably bromotrimethylphloroglucinol.

R. H. P.

Alkyl Ethers of the Phloroglucinols. III. Ethers of Dimethylphloroglucinol. By JOSEF HERZIG and M. HAUSER (*Monatsh.*, 1900, 21, 866—874. Compare preceding abstract).—By a continued treatment of an alcoholic solution of dimethylphloroglucinol with hydrochloric acid, a mixture of the mono- and di-ethyl ethers is obtained. *Dimethylphloroglucinol methyl ether* is a colourless oil which boils at 185° under 13 mm. pressure; the *dimethyl ether* crystallises in colourless needles or plates, melts at 100°, is volatile with steam, and when treated with ethyl iodide and sodium yields the *trimethyl ether* which crystallises from alcohol and melts at 59°. *Trimethylphloroglucinol ethyl ether*, obtained by repeated treatment of an alcoholic solution of trimethylphloroglucinol with hydrochloric acid, is a white, crystalline powder, melts at 130°, and when treated with bromine yields tribromotrimethylphloroglucinol (*Abstr.*, 1899, i, 32).

R. H. P.

Alkyl Ethers of the Phloroglucinols. IV. Trimethyl Ether of Phloroglucinol. By JOSEF HERZIG and H. KASERER (*Monatsh.*, 1900, 21, 875—878).—If a solution of phloroglucinol in methyl alcohol is repeatedly treated with hydrogen chloride, a small quantity of *phloroglucinol trimethyl ether* is formed; this is a white, crystalline substance, melts at 50—52°, and is volatile with steam.

R. H. P.

Influence of the Substituting Radicle on the Tautomerism of Phloroglucinol [Derivatives]. By FELIX KAUFLEDER (*Monatsh.*, 1900, 21, 993—1006).—When phloroglucinol dissolved in alcoholic potash is treated with benzyl chloride, a mixture of *phloroglucinol dibenzyl ether*, which is a yellow powder melting at 62—64°, and *phloroglucinol tribenzyl ether*, which is a similar substance melting at 39—41°, is obtained.

is obtained, and is separated by extracting the dibenzyl ether with potassium hydroxide solution. *Dimethylphloroglucinol dibenzyl ether*, which melts at 60°, and *dimethylphloroglucinol tribenzyl ether* are obtained in a similar manner from dimethylphloroglucinol. When the actions of propyl iodide and isopropyl iodide on phloroglucinol were compared, it was seen that the product from the reaction with isopropyl iodide contained a much lower proportion of the isopropyl radicle than did that from the reaction of propyl iodide of the propyl radicle. These and other differences previously known in the action of alkyl haloids on phloroglucinol are discussed. R. H. P.

Proof of the Position [of the Methyl Groups] in Dimethyl phloroglucinol Methyl Ether. By CARL BOSSE (*Monatsh.*, 1900, 21, 1021—1036).—Dimethylphloroglucinol methyl ether (Abstr., 1898, i, 579), when treated with amyl nitrite and potassium hydroxide in absolute alcohol, is converted into 5-hydroxy-3-methoxy-p-xyloquinone-4-monoxime, which forms red aggregates of crystals and melts and decomposes at 166·5°; when reduced with stannous chloride, it yields 4-amino-1 : 5-dihydroxy-3-methoxy-xylene hydrochloride, which crystallises in silky needles, forms a tetracetyl derivative melting at 137°, and, when heated with carbamide, yields 1-hydroxy-3-methoxycarbonyl-4-

aminoxynol, $\text{OH} \cdot \text{C} \begin{array}{c} \text{CMe} \cdot \text{C}(\text{OMe}) \cdot \text{C} \cdot \text{NH} \\ \parallel \quad \parallel \\ \text{C} \quad \text{C} \end{array} \text{O} \text{CO}$, which crystallises in flesh-coloured flakes and melts at 253—254°. When oxidised with ferric chloride, the hydrochloride is converted into 5-hydroxy-3-methoxy-p-xyloquinone, which crystallises in orange-coloured needles and melts at 116·5°; when reduced with stannous chloride, it yields 3-methoxy-2 : 6-dimethylphentriol, which crystallises in colourless monoclinic plates [$a : b : c = 0 \cdot 6123 : 1 : 0 \cdot 6230$, $\alpha = 125^\circ 22'$], melts at 125°, and forms a triacetyl derivative melting at 76°. The oxime previously referred to forms a sodium salt, which crystallises in ruby-red needles, and a reddish-brown silver salt; both of these, when treated with ethyl iodide, yield a small quantity of a yellowish, crystalline compound melting at 189·5°, and the ethyl ether, which crystallises in slender, yellow needles, melts at 140°, and when reduced with stannous chloride yields 4-amino-1 : 5-dihydroxy-3-methoxy-xylene hydrochloride.

R. H. P.

Action of β -Naphthol on Aldehydes. By JOHN T. HEWITT and A. J. TURNER (*Ber.*, 1901, 34, 202—204. Compare Rogoff, this vol., i, 152).—Phenyldi- β -naphtholmethane, $\text{CHPh}(\text{C}_{10}\text{H}_6 \cdot \text{OH})_2$, prepared by the action of hydrochloric acid on a solution in acetic acid of β -naphthol and benzaldehyde, crystallises from acetic acid, melts at 198° (corr.), and does not readily dissolve in any solvent but acetone. The acetate, $\text{CHPh}(\text{C}_{10}\text{H}_6 \cdot \text{OAc})_2$, forms colourless needles, melts at 199° (corr.), and is only slightly soluble in organic solvents. The anhydride, $\text{CHPh} \langle \text{C}_{10}\text{H}_6 \rangle \text{O}$, prepared by heating the dinaphthol with acetic acid at 200°, melts at 191°, and is identical with the substance prepared by Claisen (Abstr., 1887, 270) and by Trzcinski (Abstr., 1884, 1185).

T. M. L.

Symmetrical Chloride of *p*-Nitro-*o*-sulphobenzoic Acid. By WILLIAM E. HENDERSON (*Amer. Chem. J.*, 1901, 25, 1—26. Compare Remsen and Gray, *Abstr.*, 1897, i, 477; Hollis, *Abstr.*, 1900, i, 292).—The symmetrical chloride of *p*-nitro-*o*-sulphobenzoic acid melts at 98° (uncorr.), has a density of 1.85, and forms monoclinic crystals [$a:b:c = 0.898321:1:1.114179$, $\beta = 43^\circ 11' 17''$].

By the action of methyl and ethyl alcohols on this chloride, the esters described by Kastle (*Abstr.*, 1889, 711) are produced; the chloride of methyl *p*-nitro-*o*-sulphobenzoate, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{Me}) \cdot \text{SO}_2\text{Cl}$, cannot, however, be obtained from the pure symmetrical chloride, but is produced when the unsymmetrical chloride is employed. *Diphenyl p nitro-*o*-sulphobenzoate* melts at 119°, the *di-*o*-tolyl* ester at 89—90°, and the *di-*p*-tolyl* ester at 117°. When quinol is heated with the symmetrical chloride, 4 mols. of the former appear to react with 1 mol. of the latter with formation of a dark brown compound; similarly, 6 mols. of pyrogallol react with 1 mol. of the chloride. By the action of resorcinol, the *sulphone-fluorescein* of *p*-nitro-*o*-sulphobenzoic acid, $\text{O} - \text{C}[\text{C}_6\text{H}_3(\text{OH})_2]_2$, is obtained as a brown powder which exhibits a slight fluorescence in alkaline solution.

p-Nitro-*o*-sulphobenzoic anilide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{CO} \cdot \text{NHPh}) \cdot \text{SO}_2 \cdot \text{NHPh}$, crystallises in needles and melts at 222°. The *anil* melts at 183°. The *dianil*, obtained by the action of phosphorus oxychloride on the anilide, crystallises in small, yellow needles and melts at 208°; when this compound is boiled with hydrochloric acid, it is converted into the anil, whilst if heated with glacial acetic acid, the infusible anilide is produced. E. G.

***o*-Phenylsulphonebenzoic Acid and its Derivatives.** By HALL CANTER (*Amer. Chem. J.*, 1901, 25, 96—111. Compare Newell, *Abstr.*, 1898, i, 430).—*Phenyl-*o*-tolylsulphone*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2\text{Ph}$, obtained by the action of benzene and aluminium chloride on *o*-toluenesulphonic chloride, crystallises in colourless plates, melts at 67.5—68°, is readily soluble in the usual organic solvents, and also dissolves in concentrated nitric acid, but is insoluble in hydrochloric acid or water. When oxidised with hot potassium permanganate, it yields *o*-phenylsulphonebenzoic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Ph}$, in the form of small, colourless plates melting at 267—268°, and readily soluble in alcohol. The *barium* salt, with $3\text{H}_2\text{O}$; the *calcium* salt, with $4.5\text{H}_2\text{O}$; the *magnesium* salt, with $8\text{H}_2\text{O}$; the *strontium* and *zinc* salts, both with $3\text{H}_2\text{O}$, and the *cupric* salt, with $2\text{H}_2\text{O}$, are described. The *acid chloride*, $\text{CO}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Ph}$, crystallises from ether or benzene in colourless plates, melts at 262.5—263.5°, and is only sparingly soluble in the usual solvents. It is not readily decomposed by cold water, and is not volatile. The *amide* crystallises in regular, transparent plates, and melts at 220—257°; the *anilide* crystallises from alcohol in glistening plates melting at 234—235°. When the acid chloride is treated with benzene and aluminium chloride, it yields *o*-benzoyldiphenylsulphone (compare Remsen and Sanders, *Abstr.*, 1895, i, 474). J. J. S.

***o*- and *p*-Chlorophenylacetic Acid.** By H. MEHNER (*J. pr. Chem.*, 1900, 62, [ii], 554—566).—*o*-Chlorophenylacetonitrile, obtained

by the action of potassium cyanide on *o*-chlorobenzyl chloride, is a colourless oil which boils at 240—242°. When the nitrile is heated with aniline, *o*-chlorophenylacetylphenylamidine, $C_6H_4Cl \cdot CH_2 \cdot C(NHPh) : NH$, is produced, which crystallises in light brown needles and melts at 117°. The *thioamide*, $C_6H_4Cl \cdot CH_2 \cdot CS \cdot NH_2$ or $C_6H_4Cl \cdot CH_2 \cdot C(SH) : NH$, prepared by heating the nitrile with alcoholic ammonium sulphide, crystallises in white leaflets, melts at 137°, and is easily soluble in alcohol, ether, or hot water. The *amide*, obtained by the action of concentrated sulphuric acid on the nitrile, crystallises in white leaflets, melts at 175°, and dissolves readily in alcohol, hot water, or hot benzene, but only sparingly in ether. *o*-Chlorophenylacetic acid, $C_6H_4Cl \cdot CH_2 \cdot CO_2H$, prepared by the action of nitrous acid on the amide, crystallises in white needles and melts at 95°; its *ammonium* salt is described. The *anilide*, *o*-toluidide, and *p*-toluidide crystallise in white needles and melt at 138.5°, 174°, and 169.5° respectively; the *phenylhydrazide* forms white plates and melts at 175°. The *methyl* ester boils at 125—128°, and the *ethyl* ester at 134°, under 23 mm. pressure.

p-Chlorophenylacetic acid melts at 105—106°. The *anilide* crystallises in white leaflets, and melts at 164.5°; the *o*-toluidide melts at 179°, and the *p*-toluidide at 189.5°. The *phenylhydrazide* crystallises in white needles and melts at 166°. 2:5-Dinitro-*p*-chlorophenylacetic acid crystallises in pale yellow needles and melts at 167°. *Ethyl benzoyl-p*-chlorophenylacetate crystallises in white needles and melts at 97—98°. E. G.

Nitration of Mesitylenic Acid. By EUGEN BAMBERGER and ED. DEMUTH (*Ber.*, 1901, **34**, 27—33. Compare Konowaloff, *Abstr.*, 1896, i, 673).—The authors modify the details of Schmitz's method (*Abstr.*, 1879, 155) of preparing α - and β -nitromesitylenic acids, since this method, as formerly described, yields a mixture of two *dinitromesitylenic* acids (α and β).

α -Dinitromesitylenic acid [$Me_2 : (NO_2)_2 : CO_2H = 1 : 3 : 4 : 6 : 5$] is the principal product, and yields a more soluble *barium* salt than the β -acid; it forms slender, colourless prisms and melts at 212.5—213° (215.5—216° corr.). On reduction with tin and hydrochloric acid, it yields 4:6-diamino-1:3-xylene (Grevink, *Abstr.*, 1885, 144), and, with ammonium sulphide, *nitroaminomesitylenic acid* [$Me_2 : NO_2 : NH_2 : CO_2H = 1 : 3 : 4 : 6 : 5$], which crystallises from water or xylene in long, lustrous, sulphur-yellow needles, from alcohol in thick, six-sided plates, and melts at 190°.

β -Dinitromesitylenic acid [$Me_2 : (NO_2)_2 : CO_2H = 1 : 3 : 2 : 4 : 5$] crystallises from water or xylene in nodular aggregates of slender needles, melts at 207.5—208° (210.5—211° corr.), and on reduction with ammonium sulphide yields the corresponding *nitroaminomesitylenic acid* [$Me_2 : NO_2 : NH_2 : CO_2H = 1 : 3 : 2 : 4 : 5$ or $1 : 3 : 4 : 2 : 5$], which crystallises from alcohol on adding light petroleum in yellow plates and melts and decomposes at 277.5°. A small quantity of a substance melting at 175° was also obtained; this, probably, is the second nitroaminomesitylenic acid theoretically possible. *Diamino-m-xylene*, [$Me_2 : (NH_2)_2 = 1 : 3 : 2 : 4$], obtained by reducing β -dinitromesitylenic acid with tin and hydrochloric acid, yields a *dibenzoyl* derivative crystallising from abso-

lute alcohol in lustrous, white needles and melting at 226.5—227.5° (corr.). W. A. D.

Condensation of α -Benzylcinnamic Acid (Benzylidenehydrocinnamic Acid) to α -Benzylidenehydrindone. By BASTIAN SCHMID (*J. pr. Chem.*, 1900, 62, [ii], 545—553).— α -Benzylcinnamic acid dissolves slowly in concentrated sulphuric acid with formation of a yellow solution which, when poured into water, yields a crystalline precipitate of benzylidenehydrindone (Kipping, *Trans.*, 1894, 65, 498) melting at 113—114°. The *oxime* crystallises from methyl alcohol in greenish-yellow masses and melts and decomposes at 184—190°; its formation is accompanied by that of another substance which crystallises in yellow needles and melts at 155°. The *phenylhydrazone* was also prepared.

F. G.

Coumarins from Phenols and Negatively-substituted Alkyl Acetates: Study of Coumarins. By HANS VON PECHMANN and ERWIN HANKE (*Ber.*, 1901, 34, 354—362).—Ethyl benzoylacetate, when condensed with resorcinol in the presence of cold concentrated sulphuric acid, yields exclusively 4-phenylumbelliferone owing to the elimination of its acetyl group; the *benzoyl* derivative of the condensation product crystallises from alcohol in needles and melts at 136°.

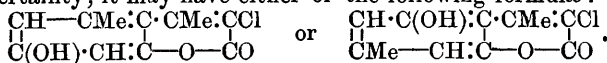
4-Methylumbelliferone results from the condensation of ethylacetylmalonate and resorcinol.

3-Chloro-4-methylumbelliferone, $\text{OH} \cdot \text{C}_6\text{H}_3 \langle \text{CMe} \rangle_{\text{O} \cdot \text{CO}} \text{C} \cdot \text{Cl}$, prepared from resorcinol and ethyl α -chloroacetate in the presence of cold concentrated sulphuric acid, separates from dilute alcohol in lustrous crystals containing $\frac{1}{2}\text{H}_2\text{O}$; it becomes anhydrous when heated at 105—110°, and then melts at 236°. The substance is somewhat insoluble even in boiling solvents, its solutions exhibiting a violet fluorescence; it dissolves in solutions of ammonia, and the alkali hydroxides and carbonates, being reprecipitated by carbon dioxide. On heating its alkaline solution, 6-hydroxy-3-methylcoumarilic acid and 6-hydroxy-3-methylcoumarin are produced.

The *acetyl* and *benzoyl* derivatives of 3-chloro-4-methylumbelliferone crystallise in leaflets and melt respectively at 161° and 163°.

3-Chlorohydroxy-4 : 1-dimethylcoumarin, produced by condensing orcinol with ethyl α -chloroacetate, crystallises in felted needles and melts at 295°; its solutions in concentrated sulphuric acid and the aqueous alkalis have a yellow colour, but no fluorescence. It differs from the preceding compound in not yielding a red coloration with ferric chloride; its *acetyl* and *benzoyl* derivatives crystallise in needles sparingly soluble in alcohol and melt respectively at 160° and 196°.

The constitution of this coumarin derivative has not been determined with certainty; it may have either of the following formulæ:



3-Chloro-4-methyldaphnetin, $\text{C}_6\text{H}_2(\text{OH})_2 \langle \text{CMe} \rangle_{\text{O} \cdot \text{CO}} \text{CCl}$, obtained by mixing an ethereal solution of ethyl α -chloroacetate and excess of pyrogallol with cold concentrated sulphuric acid, crystallises from alcohol

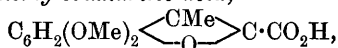
in lustrous needles and melts at 265° ; it is somewhat insoluble in the ordinary media, and its solutions do not exhibit fluorescence. The alkaline solution is yellow, and darkens on the addition of excess of solvent or on exposure to the air; ferric chloride develops a green coloration.

The *dimethyl* ether crystallises from alcohol in felted needles and melts at 172 — 173° ; on boiling with alkaline solutions, it yields 6 : 7-dimethoxy-3-methylcoumarilic acid.

The *diacetyl* and *dibenzoyl* derivatives of 3-chloro-4-methyldaphnetin crystallise respectively in prisms and needles melting at 197° and 166° . 6-Hydroxy-3-methylcoumarilic acid, produced by boiling 3-chloro-4-methylumbelliferone with excess of 10 per cent. sodium hydroxide solution, is isolated by acidifying the cooled alkaline solution and purified by crystallisation from hot water; it separates in colourless needles which at 105 — 110° evolve $\frac{1}{2}$ mol. of water, and melt at 226° . 6-Hydroxy-3-methylcoumarone is obtained as a bye-product in this reaction; it melts at 103° , and does not become coloured on exposure (compare Hantzsch, Abstr., 1886, 707).

Hydroxymethyl-4-methylcoumarone, the main product of the action of aqueous solutions of ammonia, the alkali hydroxides, or carbonates, on 3-chlorohydroxy-4 : 7-dimethylcoumarin, crystallises from water in needles melting at 94° ; it is readily soluble in the ordinary solvents, its solution is not fluorescent and does not develop any coloration with ferric chloride. The substance, when dissolved in cold concentrated sulphuric acid, develops a reddish-yellow coloration which changes to violet on heating.

6 : 7-Dimethoxy-3-methylcoumarilic acid,



obtained by boiling for 10—15 minutes 3-chloro-7 : 8-dimethoxy-4-methylcoumarin with excess of sodium hydroxide solution, crystallises from alcohol or acetic acid in lustrous leaflets and melts at 184° . In concentrated sulphuric acid, it develops a yellow coloration which changes to blue on warming.

6 : 7-Dimethoxy-3-methylcoumarone, produced by slowly distilling the preceding acid, is an oil which remains liquid at -5° and boils at 142° under 25 mm., and at 273° under the ordinary pressure; it is soluble in the ordinary solvents, and volatile in steam. Its solution in concentrated sulphuric acid is yellow and becomes blue on warming.

G. T. M.

Pseudo-acid Derived from Agaric. By L. ALPHONSE ADRIAN and AUGUSTE TRILLAT (*Compt. rend.*, 1901, 132, 151—152).—The compound, $\text{C}_{99}\text{H}_{60}\text{O}_6$, obtained by extracting powdered agaric with dilute alcohol, evaporating to dryness, and crystallising the product successively from benzene and alcohol, crystallises in needles melting at 258° (corr.); when exposed to moist air, the melting point falls to 240° . The molecular weight, determined in acetic acid solution by the ebullioscopic method, is 632, the calculated value being 624. The substance is not acidic and is only slightly soluble in sodium hydroxide solution; it dissolves in concentrated sulphuric acid without alteration,

the solution having a yellow colour which changes to orange-purple on adding a trace of nitric acid.

Fusion with potash decomposes the compound, yielding two definite products, the first a liquid boiling at 180—190° and having the properties of an unsaturated aliphatic acid, the second a neutral, pungent, aromatic oil yielding a nitro-derivative slowly decomposing at 50° but melting at 100° when rapidly heated.

The nitro-compound is insoluble in solutions of the alkalis and alkali carbonates; on reduction, it yields a diazotisable amine, the diazonium salt of which, when combined with *R*-salt gives rise to a reddish-brown azo-colouring matter.

Oxidation of the compound $C_{39}H_{60}O_6$ by chromic acid furnishes a product crystallising in white leaflets softening at 175° and melting at 185°; this substance is insoluble in solutions of the alkalis but dissolves in concentrated sulphuric acid without alteration; it contains C, 69.11, and H, 8.47 per cent. G. T. M.

Filicitanic Acid. By R. REICH (*Arch. Pharm.*, 1900, 238, 648—671).—Filicitanic acid is a glucoside contained in *Extractum Filicis maris spirituosum spissum* to the extent of 5—6 per cent.; it can be obtained from this extract by digesting with cold 10 per cent. alcohol and precipitating the filtered solution with lead acetate; it is set free from the lead precipitate by hydrogen sulphide. It is contained to the extent of 2.7 per cent. in the dried roots or rhizomes, and can be extracted directly from these with 10 per cent. alcohol; water extracts only 0.4 per cent. The substance has a faintly acid reaction; with ferric chloride, it gives a green coloration, changed to violet, and then red, by the addition of a very little sodium carbonate; it has but little reducing action on Fehling's solution or on alkaline silver salts, and in alkaline solution it is oxidised but very slowly by the air.

Filicitanic acid appears to have the composition $C_{82}H_{72}O_{36}N_2 \cdot 2H_2O$, or $C_{82}H_{76}O_{38}N_2$; its amorphous, insoluble *barium*, *calcium*, and *magnesium* salts, $C_{82}H_{70}O_{38}N_2Ba_3$, &c., were analysed. It forms a *benzoyl* derivative, $C_{82}H_{78}O_{38}N_2Bz_3$, which carbonises slowly above 200°. When dissolved in 2 per cent. aqueous potassium hydroxide and treated with bromine, it forms an orange-red *bromo*-derivative, $C_{82}H_{64}O_{38}N_2Br_{12}$. When treated with chlorine in the same way, it is at once chlorinated, oxidised, and hydrolysed (a sugar being eliminated); the product is orange-yellow, and has the composition $C_{76}H_{48}O_{30}N_2Cl_{12}$. When the acid is hydrolysed with aqueous sulphuric, hydrochloric, or hydriodic acid, a sugar is eliminated, and red, amorphous "flicx-red" is formed; this appears to be a mixture, for it is only partly soluble in alcohol. If the hydrolysis is effected with 2 per cent. alcoholic hydrochloric acid at 100°, a red, amorphous *ethyl ether*, $C_{76}H_{59}O_{29}N_2 \cdot OEt$, is obtained; this yields the same product when chlorinated as filicitanic acid does, and forms violet *magnesium* and *calcium* salts, $C_{78}H_{58}O_{30}N_2Mg_3$, &c. The *sugar* could not be obtained crystalline, nor could a crystalline derivative of it be prepared; it could not be identified with certainty, but there is a possibility that it may be dextrose. When filicitanic acid is boiled with 15 per cent. aqueous

sodium hydroxide and zinc powder, and when it is treated with alkali under other circumstances, phloroglucinol and protocatechuic acid are formed in small quantity; the main product of the reaction escaped detection, however. When the acid is oxidised with alkaline permanganate, or with nitric acid, large quantities of oxalic acid are formed; no other product could be detected. C. F. B.

Condensation of *iso*Butaldehyde with Aromatic Orthoaldehydes. By O. HERZOG and O. KRUH (*Monatsh.*, 1900, 21, 1095—1110).—*iso*Butaldehyde (Fossek, Abstr., 1884, 37) and salicylaldehyde react in the presence of dilute potassium carbonate solution or in a mixture of acetic and hydrochloric acids, yielding the unstable *aldol*,



this is a colourless oil with a phenolic odour, is sparingly soluble in water, but readily in ether or chloroform; it reduces ammoniacal silver nitrate, and when distilled under reduced pressure is resolved into its constituents. Its *oxime*, $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}$, is a pale yellow syrup, and shows few of the characteristics of oximes. When the *aldol* is treated with potassium permanganate by Zeisel's method, it is partly oxidised to a mixture of salicylic and *isobutyric* acids; with chromium trioxide, it yields a small amount of a compound melting at 64—66°, probably *o*-hydroxyisobutyrophenone, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CHMe}_2$. Alcoholic potash converts a mixture of the two aldehydes into potassium salicylaldehyde, Fossek's glycol (*loc. cit.*), and *isobutyric* acid.

o-Ethoxybenzaldehyde (Löw, Abstr., 1892, 57) and *isobutaldehyde* react under the influence of alcoholic potash to yield the *glycol*, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$, as a yellowish oil distilling at 203—205° under 16 mm. pressure, and yielding a *diacetate* which distils at 192—193° under 17 mm. pressure.

The *methoxyglycol*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$, distils at 185—186° under 16 mm., and its *diacetate* at 187° under 18 mm. pressure.

When potassium carbonate solution is used as the condensing agent, the *aldol*, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{CHO}$, is formed; it crystallises from acetone, melts and decomposes at 190—193°, is readily soluble in chloroform, and when reduced with aluminium amalgam gives the glycol described above.

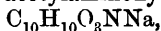
The *glycol*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$, is formed by the action of alcoholic potash on *o*-nitrobenzaldehyde and *isobutaldehyde*. After some 20 crystallisations from boiling toluene, it melts at 75°.

J. J. S.

Preparation of Aminohydroxy- and Chloroaminohydroxyketones. By FRANZ KUNCKELL (*Ber.*, 1901, 34, 124—129. Compare Abstr., 1900, i, 664).—Phenacetin readily reacts with acetyl bromide in presence of aluminium chloride to form *acetylaminohydroxyacetophenone*, $\text{NHAc} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{COMe}$, which crystallises in yellow cubes melting at 165°. The orientation of the acetyl group thus introduced has not yet been definitely ascertained, but it is probable that it takes the *o*-position to the hydroxyl. The *phenylhydrazone* melts at 207°, and the *oxime* at 160°. It is converted by nitration in acetic acid solution into

nitroacetylaminohydroxyacetophenone, $\text{NHAc} \cdot \text{C}_6\text{H}_4(\text{OH})(\text{NO}_2) \cdot \text{COMe}$, which crystallises in yellow needles melting at 170° .

The sodium derivative of acetylaminohydroxyacetophenone,

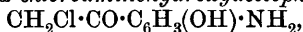


crystallises in lemon-yellow plates, melts and decomposes at 225° , and is converted by ethyl iodide into *acetylaminoethoxyacetophenone*, which crystallises in white needles melting at 155° . This substance is sometimes formed by the action of aluminium chloride on phenacetin and acetyl bromide, instead of the hydroxy-compound. When the ethoxy-compound is heated with hydrochloric acid, it yields *ethoxyaminoacetophenone* (acetyl-*p*-phenetidine), $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{COMe}$, which forms yellow needles melting at 60° . The *hydrochloride* melts at 215° , and the *phenylhydrazone* crystallises in brownish-yellow needles which decompose at 180° . *Nitroacetylaminooethoxyacetophenone* melts at 125° .

Acetylaminohydroxyacetophenone is converted by hydrochloric acid into *hydroxyaminoacetophenone* (acetyl-*p*-aminophenol),



which crystallises in yellowish needles melting at 105° , and forms a *hydrochloride* which melts and decomposes at 155° . Phenacetin is converted by chloroacetyl chloride in presence of aluminium chloride into *ω-chloroacetylaminohydroxyacetophenone*, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{C}_6\text{H}_4(\text{OH}) \cdot \text{NHAc}$, which crystallises in yellow needles melting at 190° . Hydrochloric acid converts it into *ω-chloroaminohydroxyacetophenone*,



which crystallises in yellowish-green needles, and melts at 135° . Alkalis yield with this substance an intensely red-coloured solution from which a compound of the formula $\text{C}_{20}\text{H}_{14}\text{O}_6\text{N}_2$ has been isolated.

A. H.

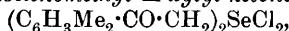
Selenium Derivatives of Aromatic Ketones. By FRANZ KUNCKELL and ROBERT ZIMMERMANN (*Annalen*, 1901, 314, 281—295. Compare Michaelis and Kunckell, *Abstr.*, 1898, i, 136).—*Selenoacetophenone*, $(\text{CPh} \cdot \text{CH}_2)_2\text{Se}$, prepared by heating selenoacetophenone dichloride with carbon disulphide and zinc dust in a reflux apparatus, crystallises from dilute alcohol in pale yellow needles and melts at 73° ; it dissolves readily in ether and in benzene, and undergoes no change when preserved. The reduction of the dichloride is effected more rapidly by the agency of potassium selenocyanide than by zinc dust. The *phenylhydrazone*, $(\text{NHPh} \cdot \text{N} : \text{CPh} \cdot \text{CH}_2)_2\text{Se}$, crystallises from dilute alcohol, and soon becomes red and viscous; it sinters at about 70° , and melts between that temperature and 100° . The *dibromide*, $(\text{CPh} \cdot \text{CH}_2)_2\text{SeBr}_2$, produced when bromine is added to an ethereal solution of the ketone, forms pale yellow needles and melts at 102° .

The *di-iodide*, $(\text{CPh} \cdot \text{CH}_2)_2\text{SeI}_2$, forms lustrous, brownish needles and melts at 112° .

When selenoacetophenone dichloride is dissolved in alcohol and heated with potassium hydroxide (2 mols.), acetophenone, selenium, and benzoic acid are produced; the last-named substance probably arises from the acetophenone by the oxidising action of selenious acid, because aqueous potassium hydroxide converts selenoacetophenone dichloride into acetophenone and selenium dioxide.

Diselenoacetophenone, $(\text{COPh}\cdot\text{CH}_2)_2\text{Se}_2$, prepared by agitating finely divided selenoacetophenone dichloride with ether and water, separates from alcohol in lustrous, yellowish crystals and melts at 125° ; hydrochloric acid precipitates selenium from the alcoholic solution, and when chlorine is passed into an ethereal solution, selenium chloride and chloroacetophenone are produced.

Seleno-p-acetylacetanilide dichloride, $(\text{COMe}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2)_2\text{SeCl}_2$, obtained from *p*-acetylacetanilide and selenium tetrachloride, is a yellow, crystalline powder which melts at 130° . *Selenomethyl anisyl ketone dichloride*, $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2)_2\text{SeCl}_2$, prepared from methyl anisyl ketone and selenium tetrachloride, forms white, silky needles and melts at 122° . *Selenopropiophenone dichloride*, $(\text{COPh}\cdot\text{C}_2\text{H}_5)_2\text{SeCl}_2$, formed when a solution of selenium tetrachloride in ether is heated with propiophenone, crystallises in white needles and melts at 124° . *Selenomethyl p-tolyl ketone dichloride*, $(\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2)_2\text{SeCl}_2$, crystallises from chloroform and melts at 132° . *Selenomethyl p-tolyl ketone*, $(\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2)_2\text{Se}$, crystallises from alcohol in slender, pale yellow needles and melts at 103° ; the *phenylhydrazone* is crystalline, but has no definite melting point, and the *dibromide* forms small, white needles which melt at 112° . *Selenomethyl m-xylol ketone dichloride*,



crystallises from chloroform in slender, white needles and melts at 128° . *Selenomethyl ψ cumyl ketone dichloride*, $(\text{C}_6\text{H}_5\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2)_2\text{SeCl}_2$, melts at 139° , and *selenomethyl cumyl ketone dichloride* at 119° . *Selenoacetyldiphenyl dichloride*, $(\text{C}_6\text{H}_5\text{Ph}\cdot\text{CO}\cdot\text{CH}_2)_2\text{SeCl}_2$, and *selenomethyl naphthyl ketone dichloride* melt at 136° and 116° respectively.

M. O. F.

Dichloroacetylcatechol and Dichloroacetylpyrogallol. By H. BRUHNS (*Ber.*, 1901, **34**, 91—97. Compare Nencki, *Abstr.*, 1895, i, 44).—Catechol and pyrogallol condense with dichloroacetic acid in the presence of zinc chloride, yielding respectively dichloroacetylcatechol (12 per cent.) and dichloroacetylpyrogallol (25 per cent.).

Dichloroacetylcatechol, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CO}\cdot\text{CHCl}_2$ [1 : 2 : 4], crystallises in prismatic plates melting at 112° and readily soluble in the usual solvents. Its alkaline solutions rapidly turn brown on exposure to the air; with ferric chloride, it gives a green coloration, which on the addition of sodium carbonate turns red. Cotton fabrics mordanted with alumina are dyed pale yellow, or with iron a gray-green. The *phenylhydrazone*, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, crystallises in glistening, yellow needles, melts at 153° , is soluble in alcohol or ether, and gradually decomposes on exposure to the air. The *semi-carbazone*, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{C}(\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$, crystallises from hot water in yellow, prismatic plates, and forms a *hydrochloride* melting at 215 — 217° which is decomposed by hot water.

Dichloroacetylpyrogallol, $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{CO}\cdot\text{CHCl}_2$ [1 : 2 : 3 : 4], crystallises from water in microscopic, rhombic prisms, melts at 165 — 166° , and dissolves readily in most organic solvents with the exception of chloroform. Its reactions are similar to those of dichloroacetylcatechol. The *phenylhydrazone*, $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, crystallises from methyl alcohol in needles melting at 235° . A *disulphonic acid*, $\text{C}_6\text{H}_4\text{O}_4\text{Cl}_2(\text{SO}_3\text{H})_2$, is obtained when the dichloro-compound

is dissolved in concentrated sulphuric acid and then diluted with a small amount of water at 0°. The *sodium* salt forms glistening needles, the *lead*, *copper*, *zinc*, and *silver* salts coloured amorphous precipitates. J. J. S.

Action of Alkalis on Chlorinated Hydroxy-ketones. By H. BRUHNS (*Ber.*, 1901, 34, 97—100).—The author cannot confirm Cassella and Co.'s statement (D.-R. P. 89602) that hydroxygalloacetophenone is obtained by the action of dilute alkalis on chlorogalloacetophenone. The action of alkalis has been studied in closed vessels in an atmosphere of hydrogen and at different temperatures, but the only products isolated were galloacetophenone and anhydroglycogallol (Nencki, *Abstr.*, 1895, i, 44).

No definite products have been obtained by the action of alkalis on chloroacetylcatechol, or the two dichloro-ketones previously described (compare preceding abstract).

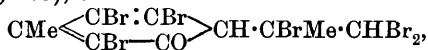
Chloroacetylcatechol reacts with semicarbazide, yielding the product $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot NH \cdot NH \cdot CO \cdot NH_2$, which crystallises in needles melting at 187°. J. J. S.

Lapachonone. III. By C. MANUELLI (*Atti Real Accad. Lincei*, 1900, [v], 9, ii, 314—318).—Bromination of lapachonone in cold acetic acid solution yields:

(1) *Bromolapachonone*, $C_{16}H_{15}O_2Br$, which crystallises from alcohol in small, sparkling, white prisms, melts at 126°, is slightly soluble in acetic acid, and gives the normal molecular weight in freezing benzene.

(2) A small quantity of a *bromodihydroxyquinone*, $C_{15}H_{15}O_4Br$, which is obtained as almost the sole product when the lapachonone is brominated in suspension in water. It separates from alcohol in heavy, lemon-yellow prisms which melt at 140° and dissolve in nearly all the common organic solvents, giving in freezing benzene the normal molecular weight. The *diacetyl* derivative crystallises from alcohol in thin, yellow plates melting at 132°; its *phenylhydrazone* separates from benzene as a red, crystalline crust which darkens in the air and assumes a greenish lustre recalling that of magenta, and on heating does not melt, but blackens at about 150° and afterwards decomposes; the *oxime* separates from benzene in minute red crystals which blacken at 140° but maintain their crystalline form even at 250°. T. H. P.

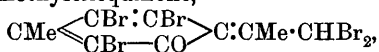
Exhaustive Bromination of Menthone. By ADOLF VON BAEYER and OTTO SEUFFERT (*Ber.*, 1901, 34, 40—53).—By the action of an excess of bromine on menthone, a crystalline product is obtained consisting chiefly of tetrabromo-*m*-cresol (10—12 per cent.) and a compound, $C_{10}H_8OBr_6$ (60 per cent.), analogous to Zincke's pseudoketobromides (*Abstr.*, 1899, i, 265), to which the formula



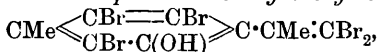
is therefore provisionally assigned; it melts and decomposes at 148—149°, crystallises from acetic acid, chloroform, or petroleum, is converted by alkalis into an intermediate red compound and then into the compounds $C_{10}H_7OBr_5$ and $C_{10}H_6OBr_4$; it also gives a red compound and loses hydrogen bromide in presence of dilute alcohol or sodium hydrogen carbonate solution or by shaking the

ethereal solution with sodium hydrogen sulphite; phenylhydrazine removes hydrogen bromide without forming a hydrazone. The *acetyl* derivative, $C_{10}H_7OBr_6Ac$, prepared by the action of cold acetic anhydride and sulphuric acid, melts and decomposes at 182° , is not acted on by hot aqueous sodium hydroxide or by silver oxide, but is converted by alcoholic sodium hydroxide into tetrabromodimethylcoumarone; the formula $CMe \begin{smallmatrix} \diagup CBr \\ \diagdown CBr \end{smallmatrix} \begin{smallmatrix} \diagup CBr \\ \diagdown C(OAc) \end{smallmatrix} \diagup CMeBr \cdot CHBr_2$ is assigned to the acetate.

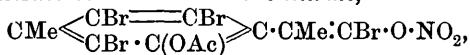
The first product of the action of alkalis on the compound $C_{10}H_8OBr_6$ is probably the methylenequinone,



but this rapidly passes into *pentabromodehydrothymol*,



which melts at 102° , dissolves readily in alkalis and in organic solvents, and is reduced to thymol by treating successively with zinc dust and alcoholic hydrogen chloride, and with sodium and alcohol. The *acetyl* derivative, $C_{10}H_6OBr_5Ac$, prepared by the action on the preceding compound of acetic anhydride containing a little sulphuric acid, or by treating the compound $C_{10}H_8OBr_6$ with acetic anhydride, crystallises from petroleum in flat, prismatic tablets, melts at 104° , and is not acted on by aqueous alkalis, but is hydrolysed by alcoholic potassium hydroxide, losing hydrogen bromide and passing into tetrabromocoumarone; silver acetate and nitrate convert it into the *nitrate*,



which melts at 89° .

Tetrabromodimethylcoumarone, $CMe : CBr \cdot \begin{smallmatrix} C \\ | \\ CBr \end{smallmatrix} \begin{smallmatrix} O \\ | \\ C \end{smallmatrix} \diagup CBr$, prepared

by the action of alkalis on any of the preceding bromination products, crystallises from chloroform in felted needles and melts at $177-178^\circ$; it is reduced by zinc dust and alcoholic hydrochloric acid to *tribromo-*

dimethylcoumarone, $CMe : CBr \cdot \begin{smallmatrix} C \\ | \\ CBr \end{smallmatrix} \begin{smallmatrix} O \\ | \\ C \end{smallmatrix} \diagup CH$, showing that one of the

bromine atoms is in the furfuran ring; this substance crystallises from glacial acetic acid in capillary needles, and melts and decomposes at $156-147^\circ$ (? $146-147^\circ$). Tetrabromodimethylcoumarone is reduced by alcohol and sodium to 2:5-dimethylhydrocoumarone.

The conversion of coumarone into *o*-ethylphenol proceeds more smoothly with hydriodic acid than with alcohol and sodium (Alexander, *Abstr.*, 1892, 1318), but the method was not successful with dimethylcoumarone. T. M. L.

Action of Sulphuric Acid on Camphor and on Camphane Dichloride. Resolution of the Camphocean Ring. By JULIUS BREDT, F. ROCHUSSEN, and J. MONHEIM (*Annalen*, 1901, 314, 369-398).—The fact that camphor, losing $1H_2O$, readily passes into cymene, led Kekulé to his formula, $CMe \begin{smallmatrix} \diagup CH \\ \diagdown CO \end{smallmatrix} \begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix} \diagup CHPr^2$, for the

ketone, this being also in agreement with the conversion into carvacrol by means of iodine. The authors now show that in both changes carvenone, $\text{CMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CO} - \text{CH} \end{smallmatrix} \text{CPr}^\beta$, is the intermediate product. The transformation of camphor into carvenone takes place under the influence of concentrated sulphuric acid at $105-110^\circ$; the unsaturated ketone is either the direct product, or, more probably, arises from dihydrocarvone, $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CO} - \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CMe} \cdot \text{CH}_2$, which readily yields carvenone under the influence of acids. Carvenone has now been isolated from the more volatile constituent of camphrene, from which previous investigation had failed to remove unaltered camphor; the separation is effected by adding phenol and distilling under reduced pressure, a molecular mixture of camphor and phenol boiling at 92° under 14 mm. pressure, whilst carvenone boils at $110-111^\circ$.

Dichlorocamphane, $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CCl}_2 \end{smallmatrix}$, also yields carvenone under the influence of concentrated sulphuric acid; it is this substance which Marsh and Gardner call camphenol (*Trans.*, 1897, 71, 290), whilst Marsh and Hartridge refer to it as carvenol (*Trans.*, 1898, 73, 852).

The experimental portion of the paper describes the production of carvenone from camphor and from dichlorocamphane, and gives details relating to the comparison of the product with carvenone.

The paper concludes with a valuable discussion of other changes involving resolution of the camphocean ring. Among these must be recognised the change which camphorquinone undergoes when treated with sulphuric acid (Manasse and Samuel, *Abstr.*, 1899, i, 300); the product consists of the isomeric quinone, $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CO} - \text{CO} \end{smallmatrix} \text{C} \cdot \text{CMe}_2$, and not, as assumed by the discoverer, of the enolic modification of camphorquinone.

In the same category the authors include the transformation of calcium camphorate into camphorone, camphoric acid into isolauronic acid, and α -campholenic acid into β campholenic acid. M. O. F.

Syntheses in the Animal Organism. II. Compounds of the Camphor Group. By HERMANN HILDEBRANDT (*Chem. Centr.*, 1901, i, 53—54; from *Arch. exp. Path. Pharm.*, 1900, 45, 110—129).—See this vol., ii, 180.

Citraptene or Lemon Camphor. By EUG. THEULIER (*Chem. Centr.*, 1901, i, 113; from *Rev. gén. chim. pur. appl.*, 3, 421—422).—When the terpenes of lemon oil are completely distilled in a vacuum, a residue is left from which, on cooling, pale yellow crystals of citraptene separate. The further purification of this substance has shown that it contains a substance which does not melt, together with two organic compounds which melt at 145° and 76° respectively. The compound of the higher melting point crystallises in yellow needles, whilst the other is present only in traces and separates from its solution in alcohol in an amorphous form. E. W. W.

Essential Oil from the Leaves of *Alpinia Malaccensis*. By PIETER VAN ROMBURGH (*Proc. K. Acad. Wetensch. Amsterdam*, 1900, 3, 451).—The leaves of *Alpinia Malaccensis*, when distilled, yielded an oil which was principally methyl cinnamate, but also contained a terpene, the nitrosylchloride of which melted at 108° and gave pinene nitrol-piperidine when treated with piperidine (pinene nitrosyl chloride melts at 103°).
R. H. P.

The Constituents of Cascarilla Oil. By GEORG FENDLER (*Arch. Pharm.*, 1900, 238, 671—690).—Cascarilla oil is obtained from the bark of *Croton eluteria*, one of the *Euphorbiaceæ*, indigenous to the Bahamas; the sample examined had the sp. gr. 0.914 at 15°, 0.911 at 20°, and $[\alpha]_D$ 4.81° at 15°.

The oil was diluted with ether, the mixture extracted with 2 per cent. aqueous sodium carbonate, and the acids so obtained separated by means of the difference of solubility of their lead salts in ether. The insoluble portion appeared to contain palmitic and stearic acids in the proportion of about 4 to 1. The soluble portion contained an acid isomeric with undecenoic acid. This acid, *cascarillic acid*, $C_{10}H_{19} \cdot CO_2H$, melts at about -15°, boils at 270°, and has a sp. gr. 0.9324 at 20°; it is an unsaturated monobasic acid of the acrylic series; its *silver* salt was analysed. It forms an oily *bromide*, and a crystalline *amide* melting at 78°. When oxidised with fuming nitric acid, it yields an unsaturated dibasic acid, $C_{11}H_{18}O_4$, melting at 111°, of which the *silver* salt was analysed; it is oxidised by permanganate to lower fatty acids.

From the remaining ethereal solution, 3 per cent. aqueous potassium hydroxide extracted a mixture of phenols, consisting of eugenol mixed with a little cresol.

No aldehyde or ketone could be isolated with sodium hydrogen sulphite. No ethereal salts are present, or mixed aliphatic-aromatic ethers.

The remaining oil, freed from ether, was distilled with alcohol. The portion that distilled over was liberated by diluting the distillate with water, and fractionated. One fraction contained a terpene, $C_{10}H_{16}$, which boils at 155—157° and 90—95° under pressures of 760 and 100 mm. respectively, has a sp. gr. 0.845 at 20°, and $[\alpha]_D$ +2.49° at 21°. It forms a *hydrochloride*, $C_{10}H_{17}Cl$, and a *bromide*, $C_{10}H_{16}Br_2$, both oily, and a *nitrosochloride*, $C_{10}H_{16}ONCl$, and a *nitrolpiperidine*, $NO \cdot C_{10}H_{16} \cdot C_2NH_{10}$, melting at 91—92° and 112° respectively. A second fraction consisted of cymene and limonene in the proportion of about 3 to 2. The portion that did not distil over with the alcohol was fractionated, and so separated into two sesquiterpenes, an alcohol, and a residue containing oxygen. One sesquiterpene, $C_{15}H_{24}$, boils at 255—257° and 178—181° under pressures of 1 atmo. and 100 mm. respectively, and has a sp. gr. 0.911 at 20°, and $[\alpha]_D$ +23.49° at 22°. The other, $C_{15}H_{24}$, boils at 260—265° and 185—190° under pressures of 760 and 100 mm. respectively, and has a sp. gr. 0.924 at 20°, and $[\alpha]_D$ +7.36° at 24°. The alcohol, $C_{15}H_{23} \cdot OH$, boils at 280—290° and 210—220° under pressures of 760 and 100 mm. respectively, and has a sp. gr. 0.977 at 20°, and $[\alpha]_D$ -7.30° at 24°; oily *acetyl* and *benzoyl* derivatives were prepared.

Cascarilla oil contains, in 100 parts: cascarillic acid, 2.0; palmitic

acid, 0.08; stearic acid, 0.02; eugenol (and cresol), 0.30; terpene, 10.0; *l*-limonene, 8.8; cymene, 13.2; sesquiterpene (255–257°), 10.5; sesquiterpene (260–265°), 33.0; alcohol, 11.0; high boiling fraction containing oxygen, 10.0; resin, 1.1 parts. C. F. B.

Essential Oil of Jasmine Blossom. V. By ALBERT HESSE (*Ber.*, 1901, 34, 291–296. Compare Abstr., 1900, i, 454, &c.).—In the 'enfleurage' of jasmine blossoms, more than 9 times as much essential oil is obtained as when the blossoms are extracted with volatile solvents. The properties of the oil obtained only from jasmine blossoms are the same as those of the oil from good commercial pomades, examined previously. Essential oil of jasmine blossom contains methyl anthranilate as a normal constituent; this appears to be formed in the 'enfleurage,' however. Small quantities of a base, resembling pyridine in character, are also present. C. F. B.

Essential Oil from *Ocimum Basilicum*. By PIETER VAN ROMBURGH (*Proc. K. Acad. Wetensch. Amsterdam*, 1900, 3, 454–455).—The leaves of the variety of *Ocimum basilicum*, called locally Selasih hidjau, yield methylchavicol when distilled; those from the variety Selasih besar yield eugenol and a terpene, "*ocimene*," which is an agreeably smelling, optically inactive liquid, boils at 73–74° under 21 mm. pressure, has a sp. gr. 0.794 at 22° and 0.801 at 15°, and n_D 1.4861; ocimene readily absorbs oxygen and resinifies. Under the ordinary pressure, it boils at 176–178° and, as also when heated in an atmosphere of carbon dioxide, is gradually converted into a liquid boiling at 195° and possessing a higher sp. gr. and stronger refraction. R. H. P.

Natural Resins [Ueberwallungsharze]. VII. By MAX BAMBERGER and EMIL VISCHNER (*Monatsh.*, 1900, 21, 949–956).—The liquid obtained by the dry distillation of pinoresinol (Abstr., 1898, i, 89) separates into an aqueous layer, which contains an undetermined aldehyde and an oily layer. When this oil is distilled under reduced pressure, guaiacol, creosol, isoeugenol and an oil, which is probably propylpyrogallol methyl ether, are obtained from successive fractions. R. H. P.

The Resin Balsam of *Pinus Pinaster* (Bordeaux Turpentine). By ALEXANDER TSCHIRCH and ED. BRÜNING (*Arch. Pharm.*, 1900, 238, 630–648).—From a solution of the turpentine in ether, 1 per cent. aqueous ammonium carbonate extracts monobasic *pimaric acid*, $C_{14}H_{22}O_2$, an amorphous substance melting at 118–119°. Aqueous sodium carbonate of 1 per cent. strength then extracts a mixture of acids, from the solution of which in methyl alcohol a relatively large amount of monobasic *pimaric acid*, $C_{20}H_{30}O_2$, crystallises; this melts at 144–146°; its *potassium, calcium, lead, and silver* salts were analysed. From the mother liquor of this acid, alcoholic lead acetate precipitates the lead salt of α -*pimarolic acid*, whilst that of β -*pimarolic acid* remains dissolved; these isomeric monobasic acids, $C_{18}H_{26}O_2$, are amorphous, and melt at 90–91° and 89–90° respectively. All these acids give the colour reactions of the sterols.

From the residual ethereal solution, the ether is distilled off, and

the residue distilled with steam. An *etheral oil* comes over; this, when distilled, yields an oil that smells like turpentine, boils at 150—175°, and has a sp. gr. 0·855 at 15°, together with a small residue of higher boiling point, which readily turns to resin. *Bordoresen* is obtained as a residue in the steam distillation; it has a viscid consistency.

The drug also contains small quantities of an *alkaloid*, and of a *colouring matter*. It has a feeble acid reaction in alcoholic solution; it neutralises no more alkali on boiling than in the cold; it contains no methoxyl group; when distilled, it yields small quantities of succinic, formic, and acetic acids.

In 100 parts of the drug there are contained: pimaric acid, 6—7; pimaric acid, 8—10; α - and β -pimaric acids, 48—50; etheral oil, easily volatile, 25—26, difficultly volatile, 3—4; resen, 5—6; succinic acid, alkaloid, colouring matter, water, and impurities, 1—2 parts.

The substances described are closely related to those obtained from Jura turpentine (this vol., i, 91). Pimaric acid is quite distinct from abietic acid; curiously enough, pimaric acid was obtained from a sample of commercial American colophonium, although an authentic resin from *Pinus palustris* was found to contain only abietic acid. The solubility of various resens in 80 per cent. aqueous chloral hydrate was also studied: canadoresen, juroresen, bordoresen, abietoresen, myroxin, β -dammaroresen, and α -alban are insoluble, whilst the others are soluble, either in the cold or on heating. The resin acids dissolve with difficulty in the cold, very readily on heating. When French turpentine oil is exposed to the air for a long time in a thin layer, but very little of a resinolic acid is formed; the main product is a resen, $C_{20}H_{34}O$, which melts at 120—130°, is homologous with juroresen, and resembles bordoresen in character.

C. F. B.

Nitrogen Derivatives of Cantharidin. By HANS MEYER (*Monatsh.*, 1900, 21, 965—980).—Cantharidinimide (Abstr., 1891,

1243), $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \\ | \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{C} - \text{CO} \cdot \text{NH} \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is easily obtained by boiling can-

tharidin with ammonia, and forms a *potassium* salt, which crystallises in lustrous leaflets, and when treated with ethyl iodide yields cantharidinethyliimide (*loc. cit.*). When the dimethyl ester of cantharidin is heated under pressure with aqueous ammonia, it is converted into a mixture of cantharidinimide and cantharidinmethyliimide. The paper concludes with a discussion of the formula of cantharidinphenylhydrazide.

R. H. P.

Anthophaein, the Brown Colouring Matter of Flowers. By M. MÖBIUS (*Chem. Centr.*, 1901, i, 190—191; from *Ber. bot. Ges.*, 1900, 18, 341—347).—The pigment contained in the black portions of the flowers of *Vicia faba* cannot be extracted by alcohol, ether, chloroform, or light petroleum, but is removed by hot water. The aqueous solution of this compound, which is named anthophaein, does not exhibit a characteristic spectrum, but forms brown precipitates with acetic, hydrochloric, nitric, sulphuric, or chromic acid. Unlike phycophain,

anthophaein may be precipitated from its aqueous solution by means of sodium chloride, magnesium sulphate, or calcium chloride.

E. W. W.

Metachlorophyllins and the Plurality of Chlorophyllins. By M. TSVETT (*Compt. rend.*, 1901, 132, 149—150).—When chlorophyll is extracted with benzene-alcohol (80 per cent.), the alcoholic extract exhibits in its spectrum only that portion of the characteristic chlorophyll band in the blue, that in the yellow, due to chlorophyllin blue, being absent; in the complete chlorophyll spectrum, it is the latter segment which predominates. These results indicate that chlorophyll contains at least two chlorophyllins.

When lime, elder, or rose leaves are macerated with alcohol, ether, chloroform, or benzene and then extracted with alcohol, the chlorophyllins in solution undergo a peculiar change and become quite insoluble in benzene, this solvent scarcely extracting any colour from the alcoholic tincture. This transformation is very rapid, and in the case of lime leaves is complete in five minutes. Dark green crystals, similar to those observed by Borodin by microchemical methods, separate on evaporating the alcoholic solution.

The names *metachlorophyllins* and *metachlorophyllin-β* are proposed for the modified chlorophyllins and the crystalline product respectively. G. T. M.

Nitrofurfuran. By R. MARQUIS (*Compt. rend.*, 1901, 132, 140—142).—*Nitrofurfuran*, $C_4OH_3 \cdot NO_2$, is obtained by nitrating furfuran dissolved in acetic anhydride at temperatures below -5° , adding the product to water, and extracting with ether containing pyridine, evaporating off the solvent under diminished pressure, and distilling the residue in a current of steam; it crystallises from light petroleum and melts at 28° . The compound has an odour resembling that of nitrotoluene; it readily dissolves in the organic solvents and in aqueous solutions of alkali hydroxides, in the latter case giving an orange solution.

The pyridine is added to the ethereal extract in order to neutralise traces of acetic and nitric acids, and also to ensure the isolation of the nitrofurfuran. When this base is not present, the final product is an oil which reduces Fehling's solution and ammoniacal silver nitrate, and combines with phenylhydrazine, yielding a compound melting at 240° . The oily substance is not distillable in steam, and when treated with boiling water it evolves nitrous fumes and yields a soluble substance with similar reducing action which gives with phenylhydrazine a compound melting at 230° . Nitrofurfuran has no reducing action and does not combine with phenylhydrazine in the cold, although combination takes place on long boiling in acetic acid solution. The oily substance, when treated with pyridine, is converted into nitrofurfuran, and the inverse transformation is effected by the action of alkalis or dilute acids. G. T. M.

Formation of Chromone Derivatives. By STANISLAUS VON KOSTANECKI and A. RÓŻYCKI (*Ber.*, 1901, 34, 102—109. Compare Nagai, *Abstr.*, 1892, 845; Tahara, *ibid.*, 846).—Bloch and Kostanecki's

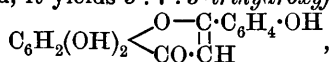
7-ethoxy-2-methylchromone (Abstr., 1900, i, 308) is obtained when Tahara's dehydroacetylresacetophenone is ethylated, and when 7-hydroxy-2-methylchromone is methylated, Nagai's dehydroacetylpaenol is formed; from these data, the authors conclude that dehydroacetylresacetophenone is identical with 7-hydroxy-2-methylchromone,

$\text{OH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CMe} \\ \parallel \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$. Dehydrodiacetylresacetophenone is probably 3-acetyl-7-hydroxy-2-methylchromone; at all events, the acetyl group is attached to carbon and not to oxygen, as there is a free hydroxyl group present.

3-Acetyl-7-ethoxy-2-methylchromone crystallises from dilute alcohol in yellowish plates melting at 130°. 7-Acetoxy-2-methylchromone forms small, thick crystals melting at 94—95°. J. J. S.

5:7:3'-Trihydroxyflavone. By STANISLAUS VON KOSTANECKI and J. STEUERMANN (*Ber.*, 1901, 34, 109—112).—2:4:6-Trimethoxybenzoyl-3'-ethoxyacetophenone, $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$, produced by the action of phloracetophenone trimethyl ether on ethyl *m*-ethoxybenzoate in presence of metallic sodium, crystallises in faintly yellow plates, melting at 100—101°. When treated with warm hydriodic acid of sp. gr. 1.7, it is converted into 5:7-dimethoxy-3'-ethoxyflavone,

$\text{C}_6\text{H}_2(\text{OMe})_2 \begin{smallmatrix} \text{O} - \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt} \\ \parallel \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$, which crystallises in silky, white needles melting at 151—152°. When this compound is boiled with concentrated hydriodic acid, it yields 5:7:3'-trihydroxyflavone,



which crystallises in microscopic needles melting at 299°, and is readily soluble in alcohol, the solution being coloured red by ferric chloride. The triacetyl derivative crystallises in needles and melts at 165—166°.

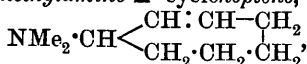
A. H.

Synthesis of Tropidine. By RICHARD WILLSTÄTTER (*Ber.*, 1901, 34, 129—144).—The complete synthesis of tropidine has been carried out from suberone as a starting point.

I. Conversion of Suberone into cycloHeptatriene.—Suberone,

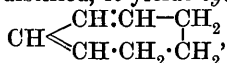
$\text{CO} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \\ \text{CH} \end{smallmatrix} \begin{smallmatrix} \text{CH}_2 \\ \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$, can readily be converted into cycloheptene,

$\text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$, which can also be obtained from cocaine. cyclo-Heptene dibromide, $\text{C}_7\text{H}_{12}\text{Br}_2$, is converted by dimethylamine in benzene solution into dimethylamino- Δ^2 -cycloheptene,



which is an oil boiling at 188° (corr.) and possessing a narcotic and penetrating odour. The platinichloride forms prisms, and melts and decomposes at 177—178°; the aurichloride melts at 94—95°, the picrate at 162—163°, and the methiodide also at 162—163°. The base combines with hydrogen chloride and with bromine, forming compounds which do not pass into ammonium compounds when heated,

The same compound is formed by the action of dimethylamine on *cycloheptadiene monohydrobromide*, and by the methylation of the amino- Δ^2 -*cycloheptene* produced by the action of bromine and an alkali on Δ^2 -*cycloheptenecarboxylamide*. When *cycloheptenetrimethylammonium hydroxide* is distilled, it yields *cycloheptadiene*,



which is identical with the *hydrotropilidene* prepared from *tropen*, and is yielded by all the three known dimethylaminocycloheptenes (methyltropans).

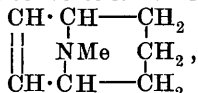
The same *cycloheptadiene* can be prepared from Δ^2 -*cycloheptenecarboxylic acid*, which can itself be obtained from *cocaine*, or indirectly from *suberone*.

Δ^1 -*cycloheptenecarboxylic acid* (prepared from *hydroxysuberanic acid*) unites with hydrogen bromide to form β -*bromocycloheptanecarboxylic acid* boiling at 167—168° under 25 mm. pressure, which on heating with *quinoline* yields a small amount of the Δ^2 -acid along with the Δ^1 -acid. The identity of the acid derived from these different sources was proved by its conversion into γ -*hydroxycycloheptanecarboxylolactone*, $\text{C}_8\text{H}_{12}\text{O}$, which crystallises in prisms melting at 103—104°.

Amino- Δ^2 -cycloheptene, $\text{NH}_2 \cdot \text{CH} \begin{array}{l} \diagup \text{CH} = \text{CH} - \text{CH}_2 \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array}$, is formed by the action of bromine and an alkali on Δ^2 -*cycloheptenecarboxylamide*, and is a mobile oil of strongly basic properties boiling at 166° (corr.). The *hydrochloride* melts and decomposes at 172—174°, the *platinichloride* at 208—210°, and the *aurichloride* at 120—121°; the *phenylthiocarbamide* melts at 129.5—130°. This base is converted by methylation into the methiodide of dimethylamino- Δ^2 -*cycloheptene*, which has been already described.

An isomeric *aminocycloheptene* is formed by the reduction of *tropilenephenylhydrazone*, and yields a *platinichloride* which melts and decomposes at 227—229°, and a *phenylthiocarbamide* which melts at 124—125°. Its constitution has not yet been ascertained.

cycloheptadiene dibromide, $\text{CHBr} \begin{array}{l} \diagup \text{CH} = \text{CH} - \text{CHBr} \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array}$, is a viscid oil boiling at 123° under 15 mm. pressure; its constitution is shown by the fact that methylamine converts it into *isotropidine*,



which can also be obtained from *bromotropen methobromide* by heating with alkalis.

cycloheptatriene, $\text{CH} \begin{array}{l} \diagup \text{CH} \cdot \text{CH} \cdot \text{CH} \\ \diagdown \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \end{array}$, can be obtained from the dibromide in two ways, by heating with *quinoline*, or by treatment with methylamine and exhaustive methylation of the resulting *tetramethyldiaminocycloheptene*, which boils at 225—235°. The hydrocarbon thus obtained is identical with the *tropilidene* prepared from *tropidine*.

II. *The Monocyclic Tropine Bases*.—Dimethylaminocycloheptadiene is formed by the action of dimethylamine on tropilidene monohydrobromide, and is identical with α -methyltropidine. *Tropilidene dihydrobromide*, $C_7H_{10}Br_2$, boils at $125-126^\circ$ under 15 mm. pressure, and differs from cycloheptadiene dibromide. The *monohydrobromide* boils at $74-75^\circ$ under 8–9 mm. pressure, and has a sp. gr. 1.4003 at $14/4^\circ$. Three of the isomeric methyltropans can also be synthetically prepared.

Δ^2 -Methyltropan has already been described as dimethylaminocycloheptene. Δ^4 -Methyltropan formed by the reduction of α -methyltropidine in alcoholic solution with sodium, boils at 189° (corr.), and has a sp. gr. 0.8866 at $14/4^\circ$. The *picrate* melts at $163-165^\circ$, and the *methiodide* at $226-227^\circ$; the *platinichloride* melts and decomposes at $178-179^\circ$. The base unites with hydrogen chloride, forming a compound which, on reduction, yields *dimethylaminocycloheptane*, $C_7H_{13} \cdot NMe_2$, which boils at 190° (corr.) and has a sp. gr. 0.8680 at $14/4^\circ$. The *platinichloride* melts and decomposes at $190-193^\circ$, and the *methiodide* decomposes at 259° . The formation of this substance renders possible the degradation of tropidine to cycloheptene, and hence its conversion into suberone.

4-Dimethylaminocycloheptanol, $NMe_2 \cdot CH \begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{OH} \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{matrix}$, is formed by the action of 20 per cent. sulphuric acid on Δ^4 -methyltropan hydrochloride, and is a viscid oil boiling at 251° (corr.).

Δ^3 -Methyltropan has previously been prepared by methylation from tropan, and is also formed by the reduction of methyltropine and by the reduction of bromotropan methobromide.

III. *Formation of Dicyclic Tropine Bases*.— Δ^4 -Methyltropan readily unites with hydrogen chloride, probably forming a mixture of the *cis*- and *trans*-modifications of the hydrochloride; when this is gently heated, a portion of it, probably the *cis*-modification, undergoes an intramolecular change, which the author terms "intramolecular methylation," and is converted into tropan methochloride, which crystallises in four-sided tablets, and forms an *aurichloride* decomposing above 290° . The remainder of the hydrochloride undergoes the same change when heated at 200° .

Synthesis of Tropidine.—Merling (Abstr., 1892, 358) has described the synthesis of tropidine by intramolecular change from α -methyltropidine hydrochloride, but the author was unable to obtain a pure tropidine derivative by this means. On the other hand, Δ^4 -methyltropan forms a dibromide which readily changes into bromo-

tropan methobromide, $\begin{matrix} \text{CH}_2 \cdot \text{CH} & \text{---} & \text{CH} \cdot \text{Br} \\ | & & | \\ \text{NMe}_2 \cdot \text{Br} & & \text{CH}_2 \\ | & & | \\ \text{CH}_2 \cdot \text{CH} & \text{---} & \text{CH}_2 \end{matrix}$, which crystallises in

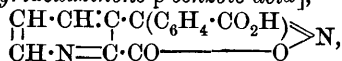
prisms. The *platinichloride* of the corresponding *methochloride* melts and decomposes at $246-247^\circ$. On heating with aqueous soda, this bromo-compound is converted into a tropidine derivative, from which pure tropidine can readily be obtained.

ψ -Methyltropine forms a dibromide which readily passes into the

isomeric ψ -bromotropanol methobromide,
$$\begin{array}{c} \text{CH}_2 \cdot \text{CH} - \text{CHBr} \\ | \quad \quad | \\ \text{NMe}_2\text{Br} \quad \text{CH} \cdot \text{OH}, \text{ which} \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CH} - \text{CH}_2 \end{array}$$

crystallises in small tablets and melts and decomposes at 237—238°. This compound can be prepared synthetically from α -methyltropan, the hydrogen chloride compound of which is converted by sodium carbonate into a base which has the properties of ψ -methyltropine, and behaves in a similar manner towards bromine. ψ -Bromotropanol methobromide is converted by most reducing agents into the original unsaturated base, but zinc and hydriodic acid convert it into tropidine methiodide. A. H.

3-*p*-Toluoylpicolinic Acid and the Products of its Oxidation. By HUGO LUDWIG FULDA (*Monatsh.*, 1900, 21, 981—992).—A continuation of the researches of Just (*Abstr.*, 1898, i, 42). 3-*p*-Toluoylpicolinic acid, when oxidised with alkaline permanganate (4 mols.) yields terephthalic acid, or (with 2 mols.) 3-*p*-carboxybenzoylpicolinic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_5\text{NH}_3 \cdot \text{CO}_2\text{H}$, which crystallises with H_2O , evolves carbon dioxide at 190°, and forms a white cadmium salt and a dimethyl ester, which crystallises in long, colourless needles and melts at 110—111°; with hydroxylamine, it yields phenylpyrid-o-oxazinone-*p*-carboxylic acid [*pyridoxazinone-p-benzoic acid*],



which is obtained as a white, crystalline powder melting and decomposing at 300°; with phenylhydrazine, it yields 1-phenyl 3-phenylquinolineazone-*p*-carboxylic [7-phenylbenzotriazin-8-one-5-*p*-benzoic] acid, $\begin{array}{c} \text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}) \\ | \quad \quad | \\ \text{CH} \cdot \text{N} = \text{C} \cdot \text{CO} - \text{NPh} \end{array} \gg \text{N}$, which is obtained as a yellowish mass, does not melt below 320°, and gives a green coloration with ferric chloride and concentrated sulphuric acid. When heated to 210°, the dicarboxylic acid loses carbon dioxide and is converted into 3-phenylpyridylketone-*p*-carboxylic acid, $\text{C}_5\text{NH}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, which crystallises in colourless, silky leaflets, melts at 267°, and forms a hydrochloride, which crystallises in yellowish needles, a white, amorphous silver salt, a cadmium salt, which crystallises, with H_2O , in clusters of leaflets, and a phenylhydrazone, which is obtained as a yellow, microcrystalline mass and melts and decomposes at 246—248°.

R. H. P.

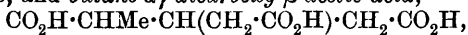
Constitution of the Cinchona Alkaloids. VI. Conversion of Cincholeuponic Acid into an Acid Free from Nitrogen. By ZDENKO H. SKRAUP (*Monatsh.*, 1900, 21, 879—912).—Cincholeuponic acid has the constitution
$$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ | \quad \quad | \\ \text{NH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2\text{H} \end{array}$$

When diethyl methylcinchleuponate methiodide (*Abstr.*, 1897, i, 99) is treated with potassium hydroxide, it is converted into diethyl dimethylcinchleuponate, which is a colourless oil boiling at 167—169° under 16 mm. pressure and forms a platinochloride, which crystallises

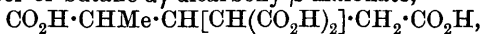
in glistening leaflets and melts at 211—212°; the corresponding *acid* may have the constitution represented by $\text{NMe}_2 \cdot \text{CH} \begin{matrix} \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2\text{H} \end{matrix}$

or $\text{CH}_2 \begin{matrix} \text{CH}_2 \text{---} \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \text{CH}(\text{NMe}_2) \cdot \text{CH} \cdot \text{CO}_2\text{H} \end{matrix}$. It is obtained as small, white, crystals, melts at 286—287°, forms an *aurichloride*, which sinters at 192° and melts at 201—202°, and, in contradistinction to its ester, is only oxidised with difficulty, it does not combine with bromine, but forms a *hydrobromide*, which melts and decomposes at 271°; when treated with methyl iodide and potassium hydroxide, the diethyl ester is converted into *diethyl trimethylcincholeuponate iodide* which is obtained in clusters of crystals, forms a *platinichloride* which crystallises in orange-yellow laminae and melts and decomposes at 220—222°, and an *aurichloride*, which crystallises in lustrous, thin leaflets and melts at 196°.

When dimethylcincholeuponic acid is fused with potassium hydroxide, dimethylamine, and *butane- α -dicarboxy- β -acetic acid*,



are obtained; this acid crystallises in monoclinic plates, melts at 138.5—140°, forms amorphous salts, and is unattacked by hydrogen iodide; it can be synthesised by warming a mixture of diethyl methylglutaconate and diethyl sodiomalonate and hydrolysing the tetraethyl ester of butane- α -dicarboxy- β -malonate,



which, when warmed with hydrochloric acid, evolves carbon dioxide and yields an acid corresponding in all its properties with that obtained from cincholeuponic acid.

R. H. P.

Derivatives of Quinolinic and Cinchomeronic Acids. By ALFRED KIRPAL (*Monatsh.*, 1900, 21, 957—964).—The acid esters previously described by the author (*Abstr.*, 1900, i, 51) as β -quinolates are really the α -compounds, since, when treated with aqueous ammonia, they yield α -quinolinamic acid (*Abstr.*, 1894, i, 301), which can be reconverted into the esters by heating them in a sealed tube with the alcohols at 100°.

Methyl α -aminonicotinate crystallises in long, white needles and melts at 85°, and when treated with aqueous ammonia yields the corresponding *amide* which crystallises in long, broad needles, melts at 195°, and can be recovered, unaltered, after heating with methyl alcohol under pressure. Monomethyl cinchomerionate (*Abstr.*, 1889, 1016, and 1900, i, 52), when treated with aqueous ammonia, yields *cinchomeronic acid*, which crystallises in prismatic tablets, melts at 170°, and when heated in a sealed tube with methyl alcohol at 100° is reconverted into methyl cinchomerionate.

R. H. P.

Chloro- and Bromo amino-derivatives of Diacetylphenylene-diamines. By FREDERICK D. CHATAWAY and KENNEDY J. P. ORTON (*Ber.*, 1900, 34, 160—167. Compare *Trans.*, 1899, 75, 1046; 1900, 77, 134, 789, 797, 800; *Abstr.*, 1900, i, 151, 152; this vol., i, 23).—All three diacetylphenylenediamines, when suspended in chloroform and

shaken with a solution of hypochlorous or hypobromous acid containing potassium hydrogen carbonate, yield the corresponding chloro- or bromoamines, $C_6H_4(NXAc)_2$ [$X = Cl$ or Br]; these, when left in contact for a long period with acetic acid, change into the isomeric substituted compounds, $C_6H_2X_2(NHAc)_2$. The transformation is complete only in the case of the meta-compounds, whilst the ortho- and para-derivatives give rise simultaneously to dark-coloured, amorphous products.

o-Diacetyldichlorodiaminobenzene, $C_6H_4(NClAc)_2$, crystallises in colourless, lustrous, four-sided prisms and decomposes explosively at about 94° ; in acetic acid solution, it is slowly converted into a diacetyldiaminodichlorobenzene [probably $(NHAc)_2:Cl_2 = 1:2:4:5$], which crystallises from alcohol in slender needles and decomposes at 290° .

o-Diacetyldibromodiaminobenzene forms irregular, yellowish prisms and explodes at $76-80^\circ$; the derived diacetyldiaminodibromobenzene [probably $(NHAc)_2:Br_2 = 1:2:4:5$] crystallises from alcohol in slender, white needles and melts and decomposes at 286° .

m-Diacetyldichlorodiaminobenzene melts at $160-161^\circ$, not at $150-151^\circ$ as stated by Morgan (Trans., 1900, 77, 1208). 4:6-Dichloro-1:3-diacetyldichlorodiaminobenzene, $C_6H_2Cl_2(NClAc)_2$, forms small, colourless prisms, melts at 127° , and decomposes at about 240° ; when boiled with glacial acetic acid, it does not undergo isomeric change, but is hydrolysed to 4:6-dichloro-1:3-diacetyldiaminobenzene.

4:6-Dibromo-1:3-diacetyldichlorodiaminobenzene forms tufts of small, lustrous, colourless prisms, melts at 181° , and decomposes at $220-230^\circ$.

m-Diacetyldibromodiaminobenzene could not be prepared owing to its rapidly undergoing further change.

4:6-Dibromodiacetylmonobromo-1:3-phenylenediamine,
 $NHAc \cdot C_6H_2Br_2 \cdot NBrAc$,

is obtained as a yellow, flocculent precipitate on adding *m*-diacetyldiaminobenzene to an excess of ice-cold hypobromous acid, containing only a small quantity of potassium hydrogen carbonate; it is always impure, and melts and decomposes at $60-70^\circ$. 4:6-Dibromo-1:3-diacetyldibromodiaminobenzene, the final product of the action of hypobromous acid on *m*-diacetyldiaminobenzene, crystallises in aggregates of sulphur-yellow prisms and melts and decomposes at 172° . When boiled with glacial acetic acid, it is hydrolysed to 4:6-dibromo-1:3-diacetyldiaminobenzene, but can be recrystallised unchanged from acetic anhydride.

p-Diacetyldichlorodiaminobenzene crystallises in small, colourless prisms and explodes at 103° . When left with glacial acetic acid at the ordinary temperature, heat is developed, and an amorphous product formed; if, however, the solution is kept cool by ice, a small quantity of 3:6-dichloro-1:4-diacetyldiaminobenzene, melting at 301° , is formed.

3:6-Dichloro-1:4-diacetyldichlorodiaminobenzene forms short, colourless prisms, decomposes at 163° , and is only hydrolysed when heated with glacial acetic acid in a sealed tube.

p-Diacetyldiaminobenzene, with hypobromous acid, fails to yield a *p*-diacetyldibromodiaminobenzene; only a yellow, amorphous substance could be isolated when decomposed at 60° , and, apparently, was diacetylmonobromo-*p*-phenylenediamine, $NHAc \cdot C_6H_4 \cdot NBrAc$, in a somewhat impure state.

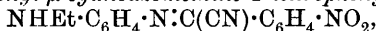
W. A. D.

Tertiary Aromatic Amines. IV. By CARL HAEUSSERMANN (*Ber.*, 1901, **34**, 38—40).—Of the two tetraphenylphenylenediamines prepared by the action of *p*-dichlorobenzene on potassium diphenylamine (*Abstr.*, 1899, i, 684), the ' α ,' melting at 199—200° is the para-compound; the ' β ,' melting at 127—129°, can be further purified by crystallising from toluene and then melts at 137·5—138°, and is identical with the product from *o*-dichlorobenzene (*Abstr.*, 1900, i, 365), yielding also an identical nitro-derivative; the product of the latter reaction is thus a meta-, and not an ortho-compound as was previously supposed.

In a similar manner, it is shown that the product obtained by the action of *o*-chlorotoluene on potassium diphenylamine is identical with that from *m*-chlorotoluene, and is not a diphenyl-*o*-toluidine, as was previously supposed, but the meta-compound. T. M. L.

Condensation of Aromatic Nitroso-compounds with Methylene Derivatives. III. By FRANZ SACHS and EDUARD BRY (*Ber.*, 1901, **34**, 118—123. Compare *Abstr.*, 1900, i, 362).—The *p*-nitroso-derivatives of the secondary bases, ethylaniline and methylaniline, react with methylene derivatives in a similar manner to the corresponding *p*-nitroso-derivatives of tertiary bases. 4-Ethylaminophenyl- μ -cyanoazomethinephenyl, $\text{NHEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{CPh}\cdot\text{CN}$, is formed by the condensation of *p*-nitrosoethylaniline and benzyl cyanide in presence of sodium carbonate, and crystallises in dark red needles melting at 112°. When heated with dilute mineral acids, it yields benzoyl cyanide and ethylphenylenediamine.

4-Ethylaminophenyl- μ -cyanoazomethine-4'-nitrophenyl,



is prepared in a similar manner from *p*-nitrobenzyl cyanide, and crystallises in silky, dichroic needles melting at 164°. 4-Methylaminophenyl- μ -cyanoazomethinephenyl, $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{CPh}\cdot\text{CN}$, crystallises in carmine-red, silky needles melting at 126°. 4-Methylaminophenyl- μ -cyanoazomethine-4'-nitrophenyl forms silky, dichroic needles melting at 188°. Ethyl 4-methylaminophenyl- μ -cyanoazomethinecarboxylate, $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, prepared from *p*-nitrosomethylaniline and ethyl cyanoacetate, crystallises in small, dichroic cubes melting at 136°.

4-Diethylaminophenyl- μ -cyanoazomethine-4'-nitrophenyl hydrochloride, $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_4\cdot\text{HCl}$, is an amorphous, lemon-yellow powder melting at 194°.

As previously described, the condensation products of *p*-nitroso-derivatives of tertiary aromatic bases with benzyl or nitrobenzyl cyanide, are decomposed by hydrochloric acid, forming a substituted phenylenediamine and a ketocyanide, whilst hydroxylamine hydrochloride yields the same base and the oxime of the ketone. Hydrazine hydrochloride acts in a similar manner to hydrochloric acid, whilst phenylhydrazine hydrochloride resembles hydroxylamine hydrochloride in its action. Thus the condensation product from *p*-nitrosodiethylaniline and benzyl cyanide, and the corresponding derivative of nitrosodimethylaniline, when treated with phenylhydrazine hydrochloride, both yield benzoyl-cyanide phenylhydrazone, $\text{CPh}(\text{CN})\cdot\text{N}\cdot\text{NHPh}$, which crystallises in yellow needles melting at 152°. This compound is not formed by the

direct action of benzoyl cyanide on phenylhydrazine, which yields benzoylphenylhydrazine. Aniline hydrochloride acts in a similar manner, but yields, as final product, the phenylamidine corresponding with the ketocyanide. Thus the condensation product of *p*-nitrosodiethylaniline with benzyl cyanide yields diphenylbenzenylamidine, $\text{NHPh}\cdot\text{CPh}\cdot\text{NPh}$, whilst that derived from *p*-nitrobenzyl cyanide yields *s*-diphenyl-*p*-nitrobenzenylamidine, $\text{NHPh}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{NPh}$, which forms a *hydrochloride* melting at 293° , but could not itself be obtained crystalline.

A. H.

A Simple Means of obtaining Secondary Symmetrical Hydrazines. By WILHELM AUTENRIETH and PAUL SPIESS (*Ber.*, 1901, 34, 187—189).—Secondary symmetrical acylhydrazines of the type $(\text{R}\cdot\text{CO}\cdot\text{NH})_2$ can be readily prepared by gradually adding the corresponding acid anhydride, $(\text{R}\cdot\text{CO})_2\text{O}$, to the calculated quantity of 50 per cent. aqueous hydrazine hydrate at 0° . *s*-*n*-Dibutyrylhydrazine, $\text{N}_2\text{H}_2(\text{COPr}^a)_2$, prepared from *n*-butyric anhydride, crystallises from dilute alcohol in lustrous, white leaflets and melts at 162 — 163° . *s*-Diisovalerylhydrazine and *s*-*n*-hexoylhydrazine are similar and melt at 184° and 159° respectively. *s*-Dibenzoylhydrazine was also prepared by this method from benzoic anhydride.

W. A. D.

Derivatives of Ethyl Phenylhydrazonocyanoacetate. By W. LAX (*J. pr. Chem.*, 1901, [ii], 63, 1—29).—Krückeberg (*Abstr.*, 1894, i, 369) has shown that the condensation products of ethyl cyanoacetate with diazonium salts exist in two isomeric modifications; when the alkaline solution of the ester is treated with carbon dioxide, the stable β -modification separates, whilst by the action of hydrochloric acid, the labile α -modification is produced. The object of the present investigation was to determine whether these substances should be regarded as azo- or hydrazone-compounds.

The β -modification of *ethyl p*-methoxyphenylhydrazonocyanoacetate, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, obtained by the action of ethyl cyanoacetate on a diazotised solution of *p*-anisidine, crystallises in long, silky, yellow needles, melts at 85° , and dissolves readily in alcohol, ether, or benzene. The α -modification melts at 116 — 118° , and by repeated crystallisation from alcohol is converted into the β -modification. The *sodium* and *silver* salts of the ester are described. When an aqueous solution of the sodium salt is treated with carbonyl chloride, condensation does not occur, but the β -modification of the ester is produced. The solubility of the α -modification in benzene at 20° is 3.87 per cent., whilst that of the β -form is 7.33 per cent.

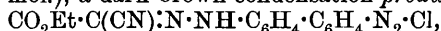
The β -modification of *ethyl o*-methoxyphenylhydrazonocyanoacetate crystallises in long needles and melts at 145° . When an alkaline solution of the ester is treated with hydrochloric acid, hydrolysis occurs with formation of the corresponding *acid*, melting at 175 — 176° . The α -modification, obtained by treating the *sodium* salt of the ester with dilute acetic acid, crystallises from ether and melts at 108° . An attempt to prepare a third modification by the action of carbon dioxide on a solution of the sodium salt at 70 — 80° (compare Weissbach, *Abstr.*, 1898, i, 366) resulted in the production of a red compound accompanied by the β -modification from which it could not be separated.

The *ammonium* and *silver* salts of the ester are described. The solubility of the α -compound in benzene at 18° is 12.09 per cent., whilst that of the β -form is 3.24 per cent.

The β -modification of *ethyl p-ethoxyphenylhydrazonocyanoacetate*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, crystallises from alcohol in large, lustrous plates, and melts at 98° . The α -compound melts at 133 — 134° ; its solubility in benzene at 20° is 2.51 per cent., whilst that of the β -form is 38.43 per cent.

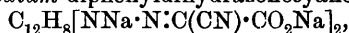
The β -modification of *methyl ethyl carboxyphenylhydrazonocyanoacetate*, $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, obtained by the action of ethyl cyanoacetate on diazotised methyl anthranilate, crystallises in small, yellow needles, melts at 155° , and is easily soluble in alcohol or ether. The α -modification melts at 139 — 140° . When the alkaline solution of the ester is heated, hydrolysis occurs, and on addition of hydrochloric acid, a yellow *acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{C}(\text{CN})\cdot\text{CO}_2\text{H}$, is obtained; its *silver* salt was prepared.

By the action of ethyl cyanoacetate (1 mol.) on a diazotised solution of benzidine (1 mol.), a dark brown condensation *product*,



is obtained which unites with β -naphthol to form *ethyl β -naphthol-azodiphenylhydrazonocyanoacetate*.

The β -modification of ethyl diphenyldihydrazonocyanoacetate (Favrel, Abstr., 1899, i, 58) melts at 208° . By the action of sodium hydroxide on the ester, *tetrasodium diphenyldihydrazonocyanoacetate*,



is produced; the corresponding *silver* salt and the *acid* were prepared, but the latter could not be obtained pure. The α -modification, obtained by the action of dilute hydrochloric acid on the *disodium* salt of the ester, melts at 233° .

The β -modification of ethyl di-*o*-tolylhydrazonocyanoacetate (Favrel, loc. cit.), prepared from the *sodium* salt of the ester, melts at 222° ; the α -modification melts at 174 — 175° , and is thereby converted into the β -form. If the sodium salt is treated with excess of hydrochloric acid, the *monoethyl* ester is produced.

Ethyl dimethoxydiphenyldihydrazonocyanoacetate, obtained by the action of ethyl cyanoacetate on a diazotised solution of dianisidine, yields an α -modification melting at 175 — 176° , and a β -modification melting at 273 — 274° ; when the former is heated above its melting point, it is converted into the latter.

Ethyl p-hydroxycarboxyphenylhydrazonocyanoacetate, prepared by the condensation of diazotised *p*-aminosalicylic acid with ethyl cyanoacetate, could not be obtained in two modifications.

When an aqueous solution of the potassium derivative of *p*-nitrophenylnitrosoamine is added to an alcoholic solution of ethyl cyanoacetate, ethyl *p*-nitrophenylhydrazonocyanoacetate is obtained identical with that prepared by Uhlmann (Abstr., 1895, i, 274) by the action of ethyl cyanoacetate on *p*-nitrodiazobenzene chloride; the α -modification melts at 177° , and the β -form at 191 — 192° . It follows, therefore, that the condensation products of ethyl cyanoacetate and diazobenzene salts must be regarded as hydrazone compounds.

Condensation products of benzidine and ethyl cyanoacetate with

phenol, resorcinol, α - and β -naphthol, and 2 : 7-dihydroxynaphthalene, and also those of *o*-tolidine and ethyl cyanoacetate, and of dianisidine and ethyl cyanoacetate with the same phenols have been prepared and their tinctorial properties examined. E. G.

New Condensation of Ethyl Diazoacetate. By EDUARD BUCHNER and C. VON DER HEIDE (*Ber.*, 1901, 34, 345—348).—*Ethyl pyrazoline-3 : 4 : 5-tricarboxylate*, $C_3N_2H_3(CO_2Et)_3$, is prepared by heating ethyl diazoacetate on the water-bath either alone or in the presence of ethyl *gem*-dimethylacrylate; it crystallises from alcohol in colourless needles and melts at 98—99°.

Ethyl pyrazole-3 : 4 : 5-tricarboxylate, $C_3N_2H(CO_2Et)_3 \cdot 2H_2O$, obtained by treating the preceding compound with 1 mol. of bromine dissolved in chloroform, crystallises from boiling water in colourless prisms and melts at 71°. The substance loses its water of crystallisation when kept in a vacuum over sulphuric acid, and the melting point rises to 91°; it is stable towards alkaline permanganate solution, whilst the preceding ester rapidly decolorises this reagent.

Pyrazole-3 : 4 : 5-tricarboxylic acid, $C_3N_2H(CO_2H)_3$, is produced by hydrolysing its ester with dilute sulphuric acid; it yields pyrazole when heated at 230—240°. The yield of pyrazole from ethyl diazoacetate is sufficiently good to warrant the use of this condensation in the preparation of the base. G. T. M.

Action of Phenylhydrazine on Aldol and on Crotonaldehyde. By GIOVANNI BATTISTA TRENER (*Monatsh.*, 1900, 21, 1111—1121).—A 40—50 percent. yield of 1-phenyl-5-methyl pyrazoline (Abstr., 1893, i, 229) is obtained when freshly prepared aldol is treated with phenylhydrazine at the ordinary temperature. Phenylhydrazine and crotonaldehyde yield the same product. If care is taken to avoid rise in temperature and the reacting substances are left in contact for 5 weeks, a polymeride, $(C_{10}H_{12}N_2)_n$, melting at 157° is formed. It is a yellow powder insoluble in alcohol or ether, and when distilled under 18 mm. pressure is reconverted into the phenylmethylpyrazoline.

1-Phenyl-5-methylpyrazoline dibromide, $C_{10}H_{12}N_2Br_2$, forms colourless crystals melting at 198°, and readily turns red on exposure to light. The *ethiodide*, $C_{10}H_{12}N_2 \cdot 2EtI$, may be obtained crystalline after several weeks; it is insoluble in chloroform and decomposes at 230° without melting. The *hydrochloride*, $C_{10}H_{12}N_2 \cdot 2HCl$, forms colourless, glistening plates but the yield is very poor.

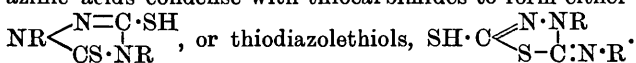
A compound, $C_{17}H_{16}N_2$, is obtained when benzaldehyde and phenylmethylpyrazoline are gently warmed for 2—3 hours; it crystallises in long, yellow prisms, melts at 140°, and is insoluble in water or acetic acid. J. J. S.

Absorption Spectra of Indophenols: Law of Auxochromic Groups containing Tertiary Nitrogen. By PAUL LEMOULT (*Compt. rend.*, 1901, 132, 142—145).—The alcoholic solutions of the indophenols derived from *p*-phenylenediamine and the phenols, and containing a primary nitrogen atom in the auxochromic group, have absorption spectra showing a brilliant red band of unabsorbed light, whilst those derived from *p*-aminodimethylaniline exhibit a less pronounced red

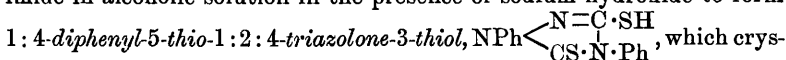
band quite distinct in position from the first. This observation is quite opposed to that of Camichel and Bayrac, who endeavour to demonstrate the fixity of the red band for all indophenols (compare this vol., i, 100). The band is fixed only when the colouring matters concerned contain the same auxochromic group, and differ only in the substituent radicles not involved in the chromophore; it is, however, very appreciably displaced on varying the radicles attached to the auxochromic nitrogen.

G. T. M.

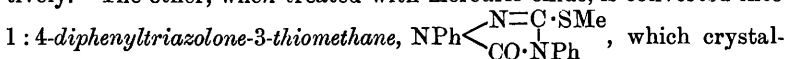
Action of Thiocarbimides on Dithiocarbazinic Acids. By MAX BUSCH and E. WOLPERT [and in part GUSTAV OBERMILLER] (*Ber.*, 1901, **34**, 304—320. Compare *Abstr.*, 1899, i, 825).—Dithiocarbazinic acids condense with thiocarbimides to form either triazolethiols,



Potassium phenyldithiocarbazinate condenses with phenylthiocarbimide in alcoholic solution in the presence of sodium hydroxide to form



treated with potassium hydroxide and methyl iodide yields the methyl ether, 1:4-diphenyl-5-thio-1:2:4-triazolone-3-thiomethane, which can be obtained in two physical modifications melting at 120° and 125° respectively. The ether, when treated with mercuric oxide, is converted into



with mercuric oxide, the disulphide, $\text{S}_2 \left(\text{C} \begin{array}{c} \text{N}-\text{NPh} \\ \diagup \quad \diagdown \\ \text{NPh}\cdot\text{CO} \end{array} \right)_2$, is obtained;

it melts at 227° and when treated with sodium amalgam yields 1:4-diphenyltriazolone-3-thiol, which crystallises from alcohol and melts at 135° . The thio-thiol, when oxidised with potassium permanganate, forms 1:4-diphenyl-5-thio-1:2:4-triazolone-3-sulphonic acid, $\text{C}_{14}\text{H}_{10}\text{N}_3\text{S}\cdot\text{SO}_3\text{H}$, which crystallises in small needles and melts at 343° , and with milder oxidising agents, such as iodine or ferric chloride, yields the disulphide, $\text{S}_2(\text{C}_{14}\text{H}_{10}\text{N}_3\text{S})_2$, which crystallises in small, yellow needles melting at $147\text{--}148^\circ$. When treated with alcoholic ammonia, the disulphide yields ammonium mercaptide and diphenylthiotriazolonylhydrothiamine, $\text{C}_{14}\text{H}_{10}\text{N}_3\text{S}\cdot\text{SNH}_2$, which crystallises in yellowish needles melting at 130° ; when treated with aniline, it forms diphenyltriazolonethioamino-

benzene, $\text{NPh} \begin{array}{c} \text{N}=\text{C}\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \\ \diagup \quad \diagdown \\ \text{CS}\cdot\text{N}\cdot\text{Ph} \end{array}$, which crystallises in yellowish

needles, melts at 175° , and forms a crystalline hydrochloride which is decomposed by water; and when treated with ethylaniline it yields diphenyltriazolonethioethylaminobenzene, $\text{C}_{14}\text{H}_{10}\text{N}_3\text{S}\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\text{Et}$, which melts at 182° , and forms a nitrosoamine crystallising in long, yellowish needles and melting at 127° ; the disulphide can also be diazotised and coupled with β -naphthol to form an azo-dye which crystallises in orange-red needles and melts at 243° .

When potassium phenylthiocarbazinate is heated alone with phenyl-

thiocarbimide, a mass is obtained which, when acidified, yields *phenylthiodiazoloneanilthiol*, $\text{SH} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{S} - \text{C} : \text{NPh} \end{smallmatrix}$; this crystallises in leaflets, melts at 171—172°, and, when oxidised with ferric chloride, yields a *disulphide* which crystallises in yellow needles and melts at 106—107°. The thiol also forms a *methyl* ether which crystallises in prismatic plates, melts at 67°, and yields a crystalline *platinichloride*; the methyl ether, when heated with hydrochloric acid, yields *phenylthiodiazolonethiomethane*, $\text{SMe} \begin{smallmatrix} \text{N} \cdot \text{N} \cdot \text{Ph} \\ \diagup \quad \diagdown \\ \text{S} - \text{CO} \end{smallmatrix}$, which crystallises in needles and can be synthesised from methyl phenyldithiocarbazine and carbonyl chloride.

The analogous *p*-tolyl and α -naphthyl compounds have been prepared in a similar manner. 1-*p*-Tolyl-4-phenyl-5-thiotriazolone-3-thiol from potassium *p*-tolylthiocarbazine crystallises in needles, melts at 162—163°, forms a crystalline *sodium* salt and a *methyl* ether which crystallises in lustrous needles and melts at 153°, and, when oxidised, yields a *disulphide* which crystallises in yellow needles and melts at 205°. *p*-Tolylthiodiazoloneanilthiol crystallises in lustrous, yellow leaflets melting at 162—163°, when oxidised yields a *disulphide* which crystallises in lustrous, yellow needles and melts at 130°, and forms a *methyl* ether which crystallises in six-sided prisms, softens at 66°, and melts at 68°. *p*-Tolylthiodiazolonethiomethane crystallises in colourless needles and melts at 52°. 1-Phenyl-4-tolyl-5-thio-1 : 2 : 4-triazolone-3-thiol, from *p*-tolylthiocarbimide and potassium phenyldithiocarbazine, crystallises in small, lustrous, yellow needles, melts at 178°, and forms a *methyl* ether which crystallises in lustrous leaflets and melts at 152°. *Phenylthiodiazolone-p*-tolylthiomethane crystallises in small tablets and melts at 101°.

4-Phenyl-1- α -naphthylthiotriazoloneethiol, from phenylthiocarbimide and potassium α -naphthylthiocarbazine, is obtained in aggregates of crystals melting at 120°, and forms a *methyl* ether which crystallises in needles and melts at 197—198°.

Phenylcarbimide and methyl phenyldithiocarbazine condense to form *methyl 2 : 4-diphenylsemicarbazide-1-dithiocarboxylate*,



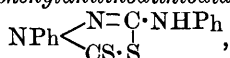
which crystallises in white needles and melts at 186°. R. H. P.

Isomeric Thiosemicarbazides. By MAX BUSCH and HERM. HOLZMANN (*Ber.*, 1901, **34**, 320—345).—The thiosemicarbazides described by Marckwald (*Abstr.*, 1893, i, 46) are shown to be, not physical isomerides, but structural isomerides of the types $\text{NH}_2 \cdot \text{NR} \cdot \text{CS} \cdot \text{NHR}$ and $\text{NHR} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHR}$, so that the compound described by Marckwald as α -diphenylthiosemicarbazide is $\beta\delta$ -diphenylthiosemicarbazide and the β -compound is $\alpha\delta$ -diphenylthiosemicarbazide. When treated with nitrous acid, the $\beta\delta$ -compound is converted into thiocarbamide, and the $\alpha\delta$ -compound into an azonitroso-compound, which is to be described later. When the $\beta\delta$ -compound is treated with benzaldehyde, it condenses to form *benzylidene- $\beta\delta$ -diphenylthiosemicarbazide*, which crystallises in yellowish needles, melts at 167—168°, decomposes at 220°, forms a crystalline *potassium* salt which sinters at (about) 180°, and a *methyl* derivative which crystallises in needles and melts at 127—128° and, when oxidised with ferric chloride, yields

diphenylthiodiazoloneanil, $\text{NPh} \cdot \text{C} \begin{array}{c} \text{NPh} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{S} \quad \text{C} \end{array} \text{Ph}$, which crystallises in lustrous, silky needles melting at $184-185^\circ$. When the $\alpha\delta$ compound is treated with benzaldehyde, a compound, $\text{C}_{20}\text{H}_{15}\text{N}_3\text{S}$, is obtained; this forms a *methiodide*, which, when treated with alcoholic potash, yields a basic compound, which crystallises in leaflets and melts at 152° .

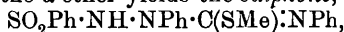
The authors ascribe the formula $\text{NPh} \begin{array}{c} \text{CH} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ >\text{O} \quad | \\ \text{C} = \text{N} \end{array}$ to the compound

obtained by Marckwald (*loc. cit.*) after oxidation with hydrogen peroxide of the substance formed by the action of carbonyl chloride on the $\beta\delta$ -compound. When treated with thiocarbonyl chloride, the $\beta\delta$ -compound yields phenylthiodiazoloneanilthiol (see preceding abstract), while the $\alpha\delta$ -compound yields *phenylanilinodithiodiazolone*,

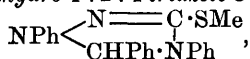


which crystallises in needles and melts at $188-189^\circ$.

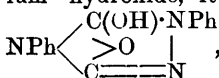
Both compounds, when treated with methyl iodide and potassium hydroxide, yield methyl ethers; the *methyl* ether of the $\beta\delta$ -compound (afterwards named the α -methyl ether), $\text{NH}_2 \cdot \text{NPh} \cdot \text{C}(\text{SMe}) \cdot \text{NPh}$, crystallises in lustrous needles, melts at $77-78^\circ$, and forms a *platinichloride* which crystallises in leaflets and decomposes at 155° , the *methyl* ether of the $\alpha\delta$ -compound (afterwards named the β -methyl ether), $\text{NHPH} \cdot \text{NH} \cdot \text{C}(\text{SMe}) \cdot \text{NPh}$, crystallises in stout needles, softens at 77° , and melts at 80° . When treated with nitrous acid, the α -ether yields the methyl ether of thiocarbonylthioanilide, whilst the β -ether yields *benzene-azophenyliminomethane-thiomethane*, $\text{NPh} \cdot \text{N} \cdot \text{C}(\text{SMe}) \cdot \text{NPh}$, which crystallises in lustrous, dark-red needles and melts at 66° . With benzene-sulphonic chloride, the α -ether yields the *sulphone*,



which forms rhombic crystals soluble in alkalis and melts at $116-118^\circ$, and the β -ether yields the *sulphone*, $\text{SO}_2\text{Ph} \cdot \text{NPh} \cdot \text{NH} \cdot \text{C}(\text{SMe}) \cdot \text{NPh}$, which is insoluble in alkalis, crystallises in leaflets, and melts at $146-147^\circ$. Carbon disulphide combines with the α -ether forming the corresponding *dithiocarbazinic acid*, $\text{CS}_2\text{H} \cdot \text{NH} \cdot \text{NPh} \cdot \text{C}(\text{SMe}) \cdot \text{NPh}$, which is obtained as a yellow, crystalline powder melting at 174° . Benzaldehyde condenses with the α -ether, giving a product identical with the ether of the benzylidene compound previously mentioned, and with the β -ether to form 1:4:5-triphenyldihydro-1:2:4-triazole-3-thiomethane,



which crystallises in six-sided tablets and melts at $108-109^\circ$. The ether of the base obtained by Marckwald by the action of carbonyl chloride on the $\beta\delta$ -compound (*loc. cit.*) can also be obtained by the action of carbonyl chloride on the α -ether; when treated with potassium hydroxide, it yields the corresponding hydroxyl compound,



, which crystallises in lustrous, flat needles, and melts at $161-162^\circ$. Carbonyl chloride reacts with the β -ether, form-

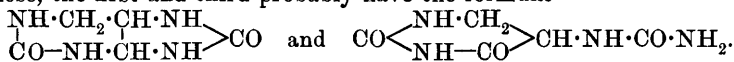
ing 1:4-diphenyltriazolone-3-thiomethane (see preceding abstract). The corresponding thio-compounds are obtained by treating the ethers

with thiocarbonyl chloride; the compound, $\text{NPh} \begin{array}{c} \text{C(SMe)·NPh} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{S} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{N} \end{array}$, crystal-

lises in short, grey needles, and melts at 156—157°. When the ethers are warmed with acetic anhydride, the α -ether is converted into phenylmethoxydiazoline (Freund and König, Abstr., 1894, i, 96), but the β -ether forms an *acetyl* derivative, which crystallises in white needles and melts at 139—140°. When treated with phenylthiocarbimide, the α -ether yields phenylanilinothiodiazoloneanil (Freund and König, *loc. cit.*), but the β -ether yields the compound

$\text{NPh} \begin{array}{c} \text{N=C·NHPH} \\ \diagup \quad \diagdown \\ \text{CS·NPh} \end{array}$, which crystallises in colourless, silky needles, melts at 179°, and when treated with methyl iodide yields a methyl derivative melting at 112—113°. R. H. P.

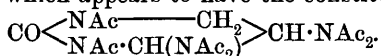
Products of the Reduction of Uric Acid. By JULIUS TAFEL (*Ber.*, 1901, 34, 258—278).—Uric acid was reduced electrolytically in sulphuric acid solution between prepared lead electrodes (Abstr., 1900, ii, 588). The uric acid must be pure, as mere traces of certain metals (platinum and mercury, for instance, but not iron) hinder the reaction greatly. Moreover, in order that crystalline products may be obtained, it is necessary that the temperature should be kept low; this is effected by immersing the lead beaker, which serves as cathode, in ice-cold water or in a freezing mixture, whilst a current of ice-cold water, or of salt solution cooled below 0°, is passed through the hollow anode. In general, unless the conditions are specially adjusted, three products are obtained, purone, *isopurone*, and tetrahydrouric acid; of these, the first and third probably have the formulæ



Some determinations of the solubility of uric acid in sulphuric acid of various strengths are given in the paper.

Purone, $\text{C}_5\text{H}_8\text{O}_2\text{N}_4$, is best obtained by electrolysis of a 10 per cent. solution of uric acid in 75 per cent. sulphuric acid at 5—8° with a current concentration of 120 amperes, freeing the solution from sulphuric acid, concentrating it under diminished pressure, and recrystallising the product from water. It decomposes rather above 250° when heated; it has practically no basic properties; it does not dissolve in cold dilute alkalis more than in water, but heating with alkalis converts it into *isopurone*; it does not decolorise permanganate or bromine water; it gives no coloration with ferric chloride; when heated with acetic anhydride, it yields eventually the same product as *isopurone* does; when heated with acids, it appears first to form *isopurone*, but eventually forms other products; when heated at 150° with aqueous barium hydroxide, it loses 2 mols. of carbon dioxide, but yields no product that could be obtained crystalline; no well characterised product could be obtained by oxidising it with nitric acid or with chlorate and hydrochloric acid.

isoPurone, $C_5H_8O_2N_4$, is best obtained by heating purone with five times its weight of 10 per cent. aqueous sodium hydroxide, previously heated to 100° , for 10 minutes at that temperature. It decomposes at 240° , appears to crystallise in two forms differing in their solubility in water, decolorises permanganate and bromine water, and gives a brownish-violet coloration with ferric chloride; it hardly dissolves in cold water, but dissolves in not too dilute alkali hydroxides, although not in alkali carbonates or in ammonia; a *nitrate*, with $1HNO_3$, and *picrate* were prepared, and the former was analysed. When boiled with acetic anhydride, it forms first a *triacetyl* derivative melting at 197° , and eventually loses carbon dioxide and forms a *substance* melting at $154-159^\circ$, which appears to have the constitution



Tetrahydrouric acid, $C_5H_8O_3N_4$, is formed in relatively larger amount when stronger acid and a low current density are employed, namely, 80 per cent. acid and a current of 15 amperes; the temperature could not then be kept lower than $20-24^\circ$. It melts and decomposes at $212-213^\circ$, does not decolorise permanganate or bromine water, is feebly acid to litmus, and dissolves in aqueous sodium hydroxide, and also in aqueous sodium carbonate or ammonia. When boiled with aqueous barium hydroxide, it loses about 1 mol. of carbon dioxide, and when heated with acids, it loses carbon dioxide and ammonia, but in neither case could crystalline products be isolated. When tetrahydrouric acid is dissolved in aqueous barium hydroxide, barium nitrite added, the mixture dropped slowly into hot dilute sulphuric acid, barium nitrate added, and the rest of the sulphuric acid removed with barium hydroxide, the filtered solution yields, when concentrated, the *nitrate* of an unstable base, $C_4H_7O_2N_3 \cdot HNO_3$; this salt decomposes at $270-290^\circ$; the *sulphate*, *picrate*, and *platinichloride*, with $2H_2O$, of the base were prepared, and the last of these was analysed. Although the nitrate is not acted on further by nitrous acid in acid solution, when it is added to a strong solution of barium nitrite, it reacts with one equivalent of the latter, and two crystalline products are formed which melt respectively at $170-180^\circ$ and 238° . C. F. B.

Products of the Reduction of Methylated Uric Acids. By JULIUS TAFEL (*Ber.*, 1901, 34, 279-291).—Various methyluric acids were reduced electrolytically to the corresponding purones by much the same method as was employed in the case of uric acid itself (preceding abstract), except that rather weaker acid was usually employed ($50-70$ per cent.), and, in the case of the tri- and tetra-methyl compounds, a lower current concentration ($10-15$ amperes). The formation of an *isopurone* in addition to a purone appears to be general; on the other hand, a compound corresponding to tetrahydrouric acid was not obtained in any case. Tetramethylpurone, however, was not accompanied by any *isopurone*, nor is it converted into an *isopurone* by treatment with an alkali; in this compound, of course, all the imino-hydrogen atoms are replaced by methyl groups. Both δ - and ζ -4-methyluric acid appear to yield the same 4-methylpurone, although the δ -pro-

duct, as actually obtained, was rather less soluble in cold water than the other.

4-Methylpurone, $C_6H_{10}O_2N_4$, decomposes rather above 260° ; *4-methylisopurone*, $C_6H_{10}O_2N_4 \cdot 2H_2O$, was also obtained in small quantity. *4:6-Dimethylpurone*, $C_8H_{12}O_2N_4$, melts and decomposes at about 240° ; the 3:4- and 1:3-isomerides were also obtained in the crystalline state. *1:4:6-Trimethylpurone*, $C_8H_{14}O_2N_4$, melts at 209° , loses 1 mol. of carbon dioxide when boiled with aqueous barium hydroxide, does not form salts with mineral acids, but forms a *picrate*, with $1C_6H_3O_7N_3$, and a *monoacetyl* derivative melting at 128.5° and 184° respectively; when heated with 10 per cent. aqueous sodium hydroxide at 100° , it is converted into *1:4:6-trimethylisopurone*, which melts at $211-212^\circ$, and gives a brownish-violet coloration with ferric chloride. *Tetramethylpurone*, $C_9H_{16}O_2N_4$, melts at 170° , loses 2 mols. of carbon dioxide when boiled with aqueous barium hydroxide, and is not converted into an *isopurone* by alkalis. C. F. B.

3-Phenyladenine. By ERNEST FOURNEAU (*Ber.*, 1901, **34**, 112—118). —Trichloro-3-phenylpurine when treated with ammonia yields as chief

product 2:5-dichloro-7-amino-3-phenylpurine,
$$\begin{array}{c} N:C(NH_2) \cdot C-N \\ | \quad | \\ CCl:N-C \cdot NPh \end{array} > CCl,$$

which forms lustrous prisms melting at 265° (corr.). This is accompanied by an isomeric *substance* melting at about 327° and a *chloro-diaminophenylpurine*, $C_{11}H_9N_6Cl$, which decomposes at about 290° . These two substances are only formed in very small quantity and have not been further investigated. 2:5-Dichloro-7-amino-3-phenylpurine is readily reduced by hydriodic acid to 3-phenyladenine,

$$\begin{array}{c} N:C(NH_2) \cdot C-N \\ | \quad | \\ CH:N-C \cdot NPh \end{array} > CH,$$
 which crystallises in lustrous tablets melt-

ing at $245-246^\circ$ (corr.) and sublimes when further heated. The *hydrochloride*, *aurichloride*, and *platinichloride* all crystallise well. Hydrochloric acid at 130° converts 2:5-dichloro-7-amino-3-phenyl-

purine into 7-amino-2:5-dioxy-3-phenylpurine,
$$\begin{array}{c} N:C(NH_2) \cdot C-NH \\ | \quad | \\ CO \cdot NH-C \cdot NPh \end{array} > CO,$$

which crystallises in colourless needles and decomposes above 285° . The *hydrochloride*, *aurichloride*, and *platinichloride* are all crystalline.

The base does not yield guanidine on oxidation with chlorine, and since it can also be obtained from the product of the action of ammonia on 5:7-dichloro-2-oxy-3-phenylpurine, it must have the constitution already given, from which that of 3-phenyladenine follows.

5:7-Dichloro-2-oxy-3-phenylpurine is converted by ammonia into a mixture of two compounds. 5-Chloro-7-amino-2-oxy-3-phenylpurine,

$$\begin{array}{c} N:C(NH_2) \cdot C-NH \\ | \quad | \\ CCl:N-C \cdot NPh \end{array} > CO,$$
 crystallises in slender needles which are

moderately soluble in hot 20 per cent. hydrochloric acid and decompose without melting at about 345° . It is converted by phosphorus oxychloride into 2:5-dichloro-7-amino-3-phenylpurine, and by hydrochloric acid into 7-amino-2:5-dioxy-3-phenylpurine. The isomeric 7-chloro-5-

amino-2-oxy-3-phenylpurine,
$$\begin{array}{c} N:CCl \cdot C-NH \\ | \quad | \\ NH_2 \cdot C:N-C \cdot NPh \end{array} > CO,$$
 decomposes with-

out melting at about 350° , and is much less soluble in hydrochloric acid than its isomeride. A. H.

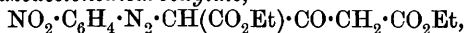
Azo-dyes from β -Naphthol and the Monosulphonic Acids of α -Naphthylamine. By GEORG VON GEORGIEVICS (*Monatsh.*, 1900, 21, 831—844).—A comparison of the properties of the seven azo-dyes obtained by coupling β -naphthol with the monosulphonic acids of α -naphthylamine. The dye from 1-naphthylamine-2-sulphonic acid crystallises in glistening needles with a greenish, metallic lustre, has a solubility of 0.14 part in 100 parts of boiling water, and gives a red coloration with ferric chloride. The dye from 1-naphthylamine-3-sulphonic acid crystallises in clusters of dark-coloured needles, has a solubility of 0.4 to 0.7 part in 100 parts of boiling water, and gives in dilute solution a violet coloration with ferric chloride. The well-known "Echthroth A" dye from 1-naphthylamine-4-sulphonic acid has a solubility of 2.6 parts in 100 parts of boiling water and gives a yellow coloration with ferric chloride. The dye from 1-naphthylamine-5-sulphonic acid is very similar to "Echthroth A," and has a solubility of 13 parts in 100 parts of boiling water. The dye from 1-naphthylamine-6-sulphonic acid crystallises in lustrous, copper-red leaflets, has a solubility of 0.5 part in 100 parts of boiling water and in dilute solution is decolorised by ferric chloride. The dye from 1-naphthylamine-7-sulphonic acid crystallises in lustrous, golden needles, and in dilute solution gives a red precipitate with ferric chloride. The dye from 1-naphthylamine-8-sulphonic acid forms lustrous, dark brown, microscopic prisms, is very similar to the dye from the 1:2-acid, has a solubility of 0.21 part in 100 parts of boiling water, and in dilute solution gives a greenish-yellow coloration with ferric chloride. These dyes further give characteristic colorations with concentrated sulphuric acid, are soluble in ethyl alcohol, slightly so in amyl alcohol, and insoluble in benzene.

The paper concludes with a description by EDUARD VALENTA of the absorption spectra of the dyes in alcoholic solution. R. H. P.

Behaviour of the Dyes obtained from the Sulphonic Acids of α -Naphthylamine and α -Naphthol with Sheep's Wool. By GEORG VON GEORGIEVICS and L. SPRINGER (*Monatsh.*, 1900, 21, 845—851).—A comparison of the colouring properties of the dyes described in the preceding abstract. The dyes are not taken up from their aqueous solutions by the wool until after the addition of acetic acid, in which they are less soluble than in water. There is no connection between the solubility of the dye and the affinity of the wool for the latter. It is probable that the dyeing of wool with these dyes does not depend on the formation of a chemical compound between the sulphonic acid and the keratin of the wool. R. H. P.

Compounds of Ethyl Acetonedicarboxylate with Diazo-compounds and their Decomposition Products. By CARL BÜLOW and WILHELM HÖPFNER (*Ber.*, 1901, 34, 71—90. Compare von Pechmann and Jenisch, *Abstr.*, 1892, 161, 162; von Pechmann, 1893,

i, 82, 84; Bamberger, 1892, 162; 1893, i, 84, 156; Bülow and Schlesinger, 1900, i, 56; Bülow, 1899, i, 271, 355; 1900, i, 65).—*Ethyl p-nitrobenzeneazacetonedicarboxylate*,



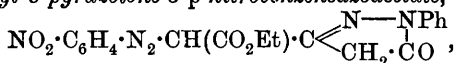
is obtained by the action of normal diazo-derivatives of *p*-nitraniline on an acetic acid solution of the ester or of the isodiazo-compounds on neutral or alkaline solutions of the esters. It forms long, yellow crystals melting at 110° , and is readily soluble in most solvents, with the exception of water; it dissolves in dilute alkalis, and may be reprecipitated by the aid of carbon dioxide, but if left too long in contact with the alkali, it is hydrolysed to a wine-red solution of *trisodium p-nitrobenzeneazacetonedicarboxylate*, which, on treatment with acetic acid, yields the yellowish-white *monosodium* salt. When the ester is boiled for 3 days with water, it yields ethyl *p*-nitroazobenzeneacetoacetate (Abstr., 1897, i, 616; 1899, i, 271). 1-Nitrophenyl-3-methyl-4-benzeneazo-5-pyrazolone, obtained by the action of *p*-nitrophenylhydrazine on ethyl benzeneazacetate, crystallises in yellow needles melting at 249° , and is only sparingly soluble in the usual solvents.

1-*p*-Nitrophenyl-3-methyl-4-*p*-nitrobenzeneazo-5-pyrazolone (Abstr., 1899, i, 272) and a small amount of *p*-nitrobenzeneazacetacetic acid are formed when the diethyl ester is hydrolysed for several days with 10 per cent. hydrochloric acid; the constitution of the dinitropyrazolone derivative thus obtained has been established by direct synthesis. Alkaline hydrolysing agents convert the diethyl ester into *anhydrous*

p-nitrobenzeneazacetonedicarboxylate, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{array}{l} \text{N} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ \text{C} \cdot \text{CH} \cdot \text{CO}_2\text{H} \end{array}$;

this crystallises from hot water in long, colourless needles melting at 251° , and is only sparingly soluble in ether, acetone, benzene, or light petroleum. When titrated with alkalis in the presence of phenolphthalein, it gives numbers indicating the presence of two carboxylic groups. The *ammonium hydrogen* salt forms colourless crystals melting at 275° and is readily soluble in water; its aqueous solution gives precipitates with the soluble salts of most of the heavy metals. The *monoethyl* ester, obtained by the action of dry hydrogen chloride on an alcoholic solution of the acid, crystallises in colourless needles melting at 180° ; it is almost insoluble in water, and dissolves but slowly in sodium carbonate or hydroxide solutions. When the acid is treated with alcoholic phenylhydrazine, it yields no hydrazone, but merely the *phenylhydrazine* salt, $\text{C}_{17}\text{H}_{15}\text{O}_6\text{N}_5$, melting at 210° .

Ethyl *p*-nitrobenzeneazacetonedicarboxylate yields a *phenylhydrazone*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{Et}) \cdot \text{N} \cdot \text{NHPh}$, in the form of red crystals melting at 160° , which readily loses alcohol, yielding two isomeric pyrazolone derivatives. *Ethyl 1-phenyl-4-p-nitrobenzeneazo-5-pyrazolone-3-acetate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH} \begin{array}{l} \text{CO} \\ \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \end{array} \begin{array}{l} \text{NPh} \\ \text{N} \end{array}$, forms red crystals melting at 189° , and only sparingly soluble in alcohol; the *acid* forms yellowish-red needles melting and decomposing at 196° , is insoluble in ether, benzene, or chloroform, and when heated slightly above its melting point loses carbon dioxide and yields 1-phenyl-3-methyl-4-*p*-nitrobenzeneazo-5-pyrazolone.

Ethyl 1-phenyl-5-pyrazolone-3-p-nitrobenzeneazoacetate,

crystallises from acetic acid in fine, yellow needles melting and decomposing at 224°, and readily soluble in glacial acetic acid or chloroform; the acid crystallises in short, green needles melting and decomposing at 205°.

Ethyl 1-carbamino-5-pyrazolone-3-p-nitrobenzeneazoacetate, obtained by the action of semicarbazide on the original condensation product, crystallises in yellow plates melting at 214—215°, and is readily soluble in acetone or hot acetic acid.

The *oxime* of ethyl *p*-nitrobenzeneazoacetonedicarboxylate crystallises in small, yellow needles melting at 160°, and dissolves in boiling acetic acid, yielding *ethyl 5-isooxazolone-3-p-nitrobenzeneazoacetate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{C} \begin{array}{l} \text{N} - \text{O} \\ \text{CH}_2 \cdot \text{CO} \end{array}$, melting at 162—163°.

Ammonia reacts with ethyl *p*-nitrobenzeneazoacetonedicarboxylate, yielding a compound, $\text{C}_{11}\text{H}_5\text{O}_5\text{N}_4$, which crystallises in red needles, melts at 296°, and is probably β -*p*-nitrobenzeneazo- α -ketoglutarimide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH} \begin{array}{l} \text{CO} - \text{NH} \\ \text{CO} \cdot \text{CH}_2 \end{array} \text{CO}$; its *phenylhydrazone*, $\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_6$, melts at 175°, and is only sparingly soluble in the usual solvents.

The original condensation product reacts partly as an azo-compound, and also as a phenylhydrazone, and hence contains a labile hydrogen atom.

J. J. S.

Explosiveness of Diazobenzenesulphonic Acid. By HERMANN WICHELHAUS (*Ber.*, 1901, 34, 11).—A case is described of violent spontaneous explosion of dry diazobenzenesulphonic acid; greater care seems necessary in dealing with it than has been hitherto thought needful.

W. A. D.

Precipitation of Proteids by Chloroform. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1900, 31, 329—337. Compare Formánek, *Abstr.*, 1900, i, 532).—Blood serum and many pathological specimens preserved with chloroform assume an opaque appearance, and in some instances a small amount of coagulated albumin is deposited. The albumin of blood serum is not all coagulated when warmed for 24—48 hours at 40° with chloroform, but at 55° the coagulation is complete in a short time. Yolk of egg when mixed with chloroform and water gradually sets to a pulp, and the filtrate from this, even when the mixture has been allowed to remain for years, contains albumin, which is coagulated on heating. Albumose solutions when preserved with chloroform also tend to coagulate, and it appears that heteroalbumose is converted into dysalbumose in contact with chloroform. The filtrate from the dysalbumose contains protalbumoses and deuteralbumoses, and chloroform is thus capable of separating primary and secondary albumoses.

The casein in milk which has been preserved with chloroform is slowly but completely precipitated.

J. J. S.

[Methylmercaptan from Albumin.] By MARCELLUS NENCKI (*Ber.*, 1901, 34, 201—202).—A claim for priority in the discovery of methylmercaptan as a decomposition product of albumin.

T. M. L.

Acid containing Phosphorus from Casein, and its Iron Compound. By ERNST SALKOWSKI (*Chem. Centr.*, 1901, i, 225; from *Centr.-Bl. med. Wiss.*, 28, 865—867).—By digesting casein with artificial gastric juice, *paranucleic acid* is formed together with paranuclein. The iron salt of this acid, prepared by heating a neutralised solution with a ferric salt, contains 22 per cent. of iron, 2.5 of phosphorus and 9 of nitrogen, and is easily assimilated by animals.

E. W. W.

Globulin as Alkali-proteid. By JOHANNES STARKE (*Zeit. Biol.*, 1900, 40, 419—446). Transformation of Albumin into Globulin. By JOHANNES STARKE (*ibid.*, 494—525).—A number of experiments are adduced to prove that globulin is an alkali-proteid, which, however, is distinguished from the albuminate usually known as alkali-albumin. It is further stated that albumin (from white of egg) can be readily transformed into globulin by diluting with water and heating to 56°.

W. D. H.

Oxidising Action of Ammonium Persulphate on Products of the Animal Organism. By LOUIS HUGOUNENQ (*Compt. rend.*, 1901, 132, 91—93).—Uric acid is oxidised by ammonium persulphate at the ordinary temperature, and converted into allanturic acid, carbamide, and glycine. In presence of an alkali hydroxide, the reaction is more energetic, but the products are carbamide and ammonium allanturate, the action being similar to that of lead or manganese peroxides, potassium permanganate or ferricyanide, or ozone. Allantoin is probably formed as an intermediate product, but if the proportion of persulphate is reduced with a view to isolate it, the greater part of the uric acid remains unaltered.

Bilirubin in presence of an alkali is completely and instantly converted into biliverdin, and the reaction affords the best method of preparing the latter.

Hæmatin in presence of ammonia is attacked in the cold, and after boiling for two or three minutes, the black solution becomes colourless and a precipitate of ferric hydroxide is formed. This reaction can be utilised for the detection of iron in hæmatin and probably also in hæmoglobin and the ferruginous nucleins.

Blood diluted and mixed with excess of ammonia is oxidised and decolorised after a few hours at the ordinary temperature with production of a pale yellow liquid and a slight ochreous precipitate. The same change is produced in a few minutes on heating.

C. H. B.

Methæmoglobin. By RUDOLF KOBERT (*Pflüger's Archiv*, 1900, 82, 603—630. Compare *Abstr.*, 1886, 637).—The best method for the preparation of methæmoglobin, is to shake a 1—4 per cent. filtered solution of blood (from carnivorous or herbivorous animals) in distilled water with a few small crystals of potassium ferricyanide in the presence

of air for a few seconds, and to decant from the undissolved ferricyanide; if oxyhæmoglobin is still present, the operation is repeated. Cow's blood gives some 10 per cent., and dog's blood 15 per cent. of methæmoglobin. In many properties, methæmoglobin resembles acid-hæmoglobin. The characteristic absorption band in the orange when measured in 0.1 per cent. solution in a layer 10 mm. thick gave 630—652 μ .

Alkali methæmoglobin obtained by the action of a few drops of very dilute solution of sodium carbonate, potassium carbonate, lime-water, basic sodium phosphate, ammonia, or an organic base, has two absorption bands near those of acid-hæmoglobin and oxyhæmoglobin, but more feebly developed. It has the same percentage composition as oxyhæmoglobin, but according to the author is a distinct substance, and in the organism is more readily reconverted into oxyhæmoglobin than is ordinary methæmoglobin.

A 1 per cent. solution of methæmoglobin spread out into a layer 3 mm. thick, and exposed to bright sunlight, is completely converted into photomethæmoglobin within 30 minutes; when placed in the dark, it is not reconverted into methæmoglobin. Most of Bock's results are confirmed.

Methæmoglobin forms an unstable compound with hydrogen peroxide, and as the combination takes place readily, the author recommends methæmoglobin as a reagent for hydrogen peroxide, the change in colour being from brown to pale red; the brown colour, however, returns when the mixture is warmed.

Szigeti and Max Richter have stated that the author's cyanomethæmoglobin (*Abstr.*, 1892, 361) is identical with Hoppe-Seyler's cyanohæmatin, but according to the author it is an entirely distinct substance.

Potassium thiocyanate changes the colour and absorption spectrum of methæmoglobin, but whether a definite compound is formed is questionable. Potassium nitrite also causes a change in colour from brown to red.

The existence of a sulphomethæmoglobin is questioned.

Even dilute solutions of hæmoglobin and its derivatives exhibit strong absorption bands in the violet and ultra-violet of the spectrum.
J. J. S.

Decomposition Products of Oxyhæmoglobin from Horses. By D. LAWROFF (*Ber.*, 1901, 34, 101—102. Compare *Abstr.*, 1899, ii, 231).—Some 20.3 per cent. of hexon bases are obtained by the action of hydrochloric acid and tin on oxyhæmoglobin from horses; the bases consist of histidine, arginine, and lysine.
J. J. S.

Mechanism of the Action of Enzymes. By MAURICE HANRIOT (*Compt. rend.*, 1901, 132, 146—149).—When an enzyme is attenuated by chemical action, it can be regenerated and return to its former activity. The action of lipase on acids and ethers appears to be a chemical combination which obeys the laws of dissociation.

W. D. H.

Action of Nitrous Acid on Wool. By ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 766—774).—The action which hot nitric acid exerts on wool with the production of a yellow colour is

found to be due to the nitrous acid formed when the nitric acid is heated, the intensity of the colour increasing with the proportion of nitrous acid present. The colour which nitric acid imparts to wool is, however, perfectly stable towards sunlight, whilst that given by nitrous acid undergoes rapid change, unless the wool be subsequently dipped into cold nitric acid, when the colour becomes stable to light. Experiments made on the change of weight occurring when wool is nitrated showed in the majority of cases a loss of weight varying between 2.19 and 21.9 per cent., although in one case an increase of 1.98 per cent. was observed. The nitrated wool feels coarser to the touch than before treatment, and reacts readily in the cold with ordinary reducing reagents, the yellow colour being converted into a dark brown. The nitrated wool, after perfect washing, is acid towards litmus, and at a temperature of 50—60° decomposes carbonates with the evolution of carbon dioxide, the colour of the wool being changed to brown. It darkens when heated in a vacuum at 110—120° and afterwards chars; it is comparatively readily acted on by dyes. Nitrated wool decomposes potassium iodide solution, with precipitation of iodine, both in the fibre and in the solution. The coefficient of acidity (the number of milligrams of potassium hydroxide fixed by 1 gram of the substance when acted on by seminormal alcoholic potassium hydroxide for 12 hours) of the unaltered wool has a mean value 88, whilst that of the nitrated product is 169. If the nitrated wool after absorption of potassium hydroxide be washed with alcohol until it has a neutral reaction, it will be found to be strongly alkaline on placing in water, owing to the hydrolysis of the unstable alkali compound. Nitrated wool is not hygroscopic, and it contains less nitrogen than the raw material. The iodine values for wool before and after nitration have the mean values 18.4 and 4.7 respectively. The action of nitrous acid on wool may be regarded partly as a saturation of the free bonds of the molecule with nitro- or nitroso-groups, and partly as an action of nitrous acid on the amino-groups present, to which is due the increase produced in the acid functions.

T. H. P.

Mercury Organo-metallic Compounds. By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and CHEVROTIER (*Compt. rend.*, 1901, 132, 145—146).—*Sodium mercuriphenoldisulphonate*, prepared by treating sodium phenoldisulphonate with mercuric oxide in mol. proportion, is an amorphous, white powder containing about 40 per cent. of mercury; 22 parts of the salt dissolve in 100 parts of water at 15°. A solution of this compound is salt to the taste like that of a sodium salt; it yields no precipitates with sodium hydroxide, hydrochloric acid, ammonium hydrosulphide, or cold albumin solution. The substance possesses the germicidal and antiseptic properties of a mercury salt without its irritating action on the animal membranes. Solutions containing 1/1000th to 1/2000th parts of the compound stop the development of Eberth's bacillus, *B. pyocyaneus*, *B. staphylococcus*, *B. subtilis*, and *B. lactis*, and prevents the putrefaction of blood, meat-infusion or urine. The coefficient of toxicity determined for the rabbit by intravenous injection is 0.039 gram per kilo.; that for the guinea pig by subcutaneous injection is 0.05 gram per kilo.

G. T. M.

Organic Chemistry.

Generation of Hydrocarbons by Metallic Carbides. By M. BERTHELOT (*Compt. rend.*, 1901, 132, 281—290).—Of the various types of metallic carbides the acetylides are the simplest, being derived from acetylene by the substitution of the hydrogen atoms by two atoms of a univalent, or one atom of a bivalent, metal. Some of these are decomposed by water with the development of heat and the regeneration of acetylene. The condition for the occurrence of this reaction is that $r - q > 196.1$, where r is the heat of formation of the acetylide from its elements, and q that of the metallic hydroxide. This condition is fulfilled by the carbides of sodium, lithium, calcium, &c., but not by that of silver. Silver carbide is, however, decomposed by dilute hydrochloric acid, the reaction being rendered possible by the increased development of heat due to the formation of silver chloride. If the alkali acetylide contains an excess of metal, the latter decomposes the water with the formation of hydrogen, which immediately reduces the acetylene to ethane and ethylene, all these reactions taking place with the development of heat. A mixture of acetylene, ethylene, and ethane is thus produced, the relative proportions of these gases being dependent on local conditions. A similar formation of ethylene takes place when cuprous acetylide is decomposed by acids in the presence of zinc. Certain metallic oxides, capable of decomposing water, under certain conditions, with the development of heat, also effect the transformation of acetylene into ethylene. Thus ammoniacal solutions of chromous salts absorb acetylene, and then, almost immediately, evolve ethylene.

Aluminium carbide, Al_4C_3 , may be taken as the type of a second class of carbides which are decomposed by water, with the production of methane instead of acetylene. In the case of aluminium carbide, the reaction takes place so slowly that the heat developed cannot be estimated directly, but an approximate value may be calculated from the heat of combustion of the carbide, which was found to be +824 Cal. It is shown from a comparison of thermochemical data that the formation of methane from aluminium carbide corresponds with the greatest possible development of heat. The author lays stress on two principles involved in reactions such as those under consideration, namely, the conservation of the molecular type resulting from the exchange of equal valencies and the tendency towards the production of the maximum thermal effect. Both these principles are satisfied in the decomposition by water of aluminium carbide and, probably, of beryllium carbide, which also furnishes pure methane.

A third class of carbides includes that of manganese, Mn_3C , which furnishes equal volumes of methane and hydrogen, and here also it is shown that the production of acetylene, ethylene, or ethane would result in the development of less heat than that actually observed.

The reactions involved in the decomposition of the carbides of cerium, lanthanum, yttrium, uranium, &c., are more complex, variable

mixtures of methane, acetylene, ethylene, and small quantities of liquid hydrocarbons being produced. These results are attributed partly to the fact that the composition of the oxides of the metals referred to does not correspond with that of the carbides; possibly, also, the latter are mixtures or polymerised compounds. N. L.

Composition of Grosny Naphtha. By MICHAEL I. KONOWALOFF and MME. A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 50—51).—By the action of concentrated sulphuric acid on a fraction of Grosny naphtha boiling at 160—165°, a considerable proportion of sulphomesitylenic acid was obtained, together with a crystalline compound melting at 210°. The fraction hence contains a large quantity of mesitylene. T. H. P.

Action of Organometallic Derivatives on Alkyl Esters. By AUGUSTE BÉHAL (*Compt. rend.*, 1901, **132**, 480—482).—When alkyl-halogen magnesium compounds act on alkyl esters of the cyclic series, the first stage in the reaction is $R \cdot CO_2Et + MgMeI = MgI \cdot O \cdot CRMe \cdot OEt$, and the second stage $MgI \cdot O \cdot CRMe \cdot OEt + MgMeI = MgI \cdot OEt + MgI \cdot O \cdot CRMe_2$. Finally, $MgI \cdot O \cdot CRMe_2 = MgI \cdot OH + CRMe : CH_2$, possibly with intermediate formation of the tertiary alcohol. The ethylenic hydrocarbons thus obtained polymerise readily, forming crystalline solids. When oxidised with chromic mixture or permanganate, they yield methyl ketones, and when treated with iodine and mercuric oxide in presence of alcohol, they also yield methyl ketones and not aldehydes, $CRMe \cdot CH_2 \cdot OH = HI + R \cdot CH_2 \cdot COMe$.

C. H. B.

Mode of Addition of Hypochlorous Acid to the Olefines. By K. KRASSUSKY (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 1—26).—The author has studied the additive products obtained by the combination of hypochlorous acid with the olefine hydrocarbons, *isobutylene*, propylene, and β -methyl- β -butylene. His results confirm the law enunciated in 1876 by Markownikoff, to the effect that when hypochlorous acid combines with an ethylene derivative, the hydroxyl group becomes joined preferably to the carbon atom with which are united the fewest hydrogen atoms. Under unfavourable conditions, the reaction gives rise to secondary products formed by the action of water, acid, and chlorine on the chlorohydrin and the hydrocarbon. The concentration of the hypochlorous acid used has not much influence on the course of the reaction, which, however, depends to some extent on the temperature.

The action of hypochlorous acid on *isobutylene* gives a yield of about 78 per cent. of the theoretical quantity of the chlorohydrin, $OH \cdot CMe_2 \cdot CH_2Cl$, which boils at 126—128° and has the sp. gr. 1·0878 at 0°/0° and 1·0687 at 17·6°/0°. If strong hypochlorous acid is used, the chlorohydrin is accompanied by a considerable proportion of an unsaturated chloro-derivative boiling at 69—70° and having the composition C_4H_7Cl , which is also obtained when *isobutylene* chlorohydrin is heated either with anhydrous oxalic acid or by itself in a sealed tube.

β -Methyl- β -butylene and hypochlorous acid give a 25 per cent. yield of the chlorohydrin, $\text{OH}\cdot\text{CMe}_2\cdot\text{CHMeCl}$, which boils at $141\text{--}142^\circ$, and has the sp. gr. $1\cdot0546$ at $0^\circ/0^\circ$ and $1\cdot0356$ at $18\cdot6^\circ/0^\circ$.

By the action of anhydrous oxalic acid or phosphoric oxide, β -methyl- β -butylene chlorohydrin is converted into β -methyl- γ -chloro- β -butylene, $\text{CMe}_2\cdot\text{CMeCl}$, which boils at $97\text{--}98^\circ$ and has the sp. gr. $0\cdot9395$ at $0^\circ/0^\circ$ and $0\cdot9215$ at $18\cdot1^\circ/0^\circ$. The addition of bromine to the latter compound gives rise to a solid bromo-derivative, $\text{C}_5\text{H}_9\text{ClBr}_2$, which has the normal molecular weight in freezing benzene.

T. H. P.

Complete Synthesis of Acetylpropylene [Pentinene] and of Terpilenic Hydrocarbons. By MARCELLIN BERTHELOT (*Compt. rend.*, 1901, 132, 599—606).—When a mixture of equal volumes of acetylene and propylene is heated at about 500° for an hour, a contraction of about one-third takes place, and a nearly colourless, oily liquid, together with a little tarry matter, condenses in the colder parts of the vessel. The greater part of the condensed liquid is readily volatile, and consists of a pentinene, C_5H_8 , whilst the smaller, less volatile portion appears to consist of terpilenic hydrocarbons; benzene is not formed in appreciable quantity unless the gases have been too strongly heated. The residual gases, amounting to 63·9 per cent. of the original volume, contained unaltered acetylene and propylene, each 23 vols.; gaseous pentinene, 9 vols.; methane (or an equivalent mixture of saturated hydrocarbons with hydrogen), 8·9 vols.

Similar results are obtained by heating a mixture of acetylene and trimethylene, the latter probably first being transformed into the isomeric propylene. With a mixture of allylene and ethylene, combination also occurs, but more slowly; the liquid product of the reaction consists of hydrocarbons of high boiling point, together with a small quantity of a volatile hydrocarbon, probably allylethylene, isomeric with the preceding pentinene. Allylene and acetylene enter into reaction much more readily, a liquid rich in benzene being obtained, besides an abundance of tarry matter. Propylene and ethylene react very slowly, only a trace of liquid being formed. The final step in the synthesis of terpilenic hydrocarbons is to be sought in the polymerisation and interaction of the two pentinenes already referred to and their isomerides, these being formed, as described above, from hydrocarbons which may themselves be synthetically formed from their elements.

N. L.

$\alpha\delta$ -Dibromobutane and $\alpha\delta$ -Diiodobutane. New Synthesis of Adipic Acid. By JULES HAMONET (*Compt. rend.*, 1901, 132, 345—347).— $\alpha\delta$ -Dibromobutane, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, readily formed by saturating $\alpha\delta$ -diamyloxybutane with hydrogen bromide, is a colourless liquid which boils, and partially decomposes, at $196\text{--}197^\circ$, and has a sp. gr. $1\cdot79$ at 18° . $\alpha\delta$ -Diiodobutane, obtained in a similar manner with almost the theoretical yield, boils with slight decomposition at $125\text{--}126^\circ$ under 15 mm. pressure, and has a sp. gr. $2\cdot307$ at 18° . When treated with potassium cyanide, and the resulting nitrile hydrolysed, adipic acid is obtained.

N. L.

Pyrogenic Reactions of Organic Compounds. By WLADIMIR IPATIEFF (*Ber.*, 1901, **34**, 596—600. Compare Marchand, *J. pr. Chem.*, 1838, **15**, 7; Caventon, *Annalen*, 1863, **127**, 93).—When methyl alcohol is passed through a red hot iron tube, considerable quantities of formaldehyde are produced together with combustible gases and about 3 per cent. of carbon. When ethyl alcohol is passed through a glass tube heated at 660—700°, very little decomposition occurs, but when an iron tube heated at 710—750° is employed, considerable amounts of acetaldehyde, paraldehyde and combustible gases are formed together with about 3 per cent. of carbon. *iso*Butyl alcohol under similar conditions gives about 40 per cent. of pure *isobutylaldehyde* and *iso*amyl alcohol 30—40 per cent. of the corresponding aldehyde. The author recommends the method as a simple one for the preparation of aldehydes.

Methyl*isobutyl*carbinol gives a 30—40 per cent. yield of methyl *isobutyl* ketone. Tertiary alcohols appear to be more stable, thus when dimethylethylcarbinol is passed through an iron tube heated at 660—700°, the greater part remains unaltered, but at 750—800° an olefine hydrocarbon, water, and combustible gases are produced.

J. J. S.

Action of Alcohol on Metals. By MALMÉJAC (*J. Pharm.*, 1901, [vi], **13**, 169—171).—Iron, tin, zinc, lead, and galvanised iron were allowed to remain in contact with alcohol of 95° for six months at 15°, when it was found that in all cases a small quantity of the metal had gone into solution. Copper, under the same conditions, is entirely unacted on.

H. R. LE S.

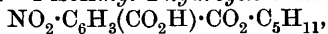
Separation of the Amyl Alcohols contained in Fusel Oil. I. By WILLY MARKWALD (*Ber.*, 1901, **34**, 479—484. Compare Pasteur, *Compt. rend.*, 1855, **41**, 296; Le Bel, this Journal, 1874, 139; *Bull. Soc. Chim.*, 1874, [ii], **21**, 542; 1876, [ii], **25**, 545; Rogers, *Trans.*, 1893, **63**, 1130; Balbiano, this Journal, 1877, i, 292).—The reason that the separation of the two amyl alcohols by Pasteur's method is so tedious is that the two barium salts form mixed crystals; the separation of the two salts could probably be more readily accomplished by other methods. Le Bel was in error in assuming that a limit was reached when the quantities of the two amyl alcohols in the mixture were in the inverse ratio of their esterification constants with hydrogen chloride. Using Rogers' data, the ratio of the velocities of esterification of the two amyl alcohols may be calculated, and is found to be $c = 0.446$. It is pointed out that if Rogers had completed the process used by him only 30 c.c. of 99 per cent. active amyl alcohol would have been obtained from 16.2 litres of commercial amyl alcohol.

The amount of active alcohol present in the commercial product varies (16.5—27 per cent.), but at the present time the percentage does not appear to be so high as formerly (Ley, *Ber.*, 1873, **6**, 1362).

J. J. S.

Separation of the Amyl Alcohols contained in Fusel Oil. II. By WILLY MARKWALD and ALEXANDER MCKENZIE (*Ber.*, 1901, **34**, 485—491. Compare preceding abstract).—The authors have

succeeded in separating the two amyl alcohols of fusel oil, *iso*amyl alcohol and β -methylbutyl alcohol, by converting them into acid esters of 3-nitrophthalic acid (compare Wegscheider and Lipschitz, this vol., i, 32). The separation of the two esters is tedious, as they form mixed crystals. 1-*iso*Amyl 2-hydrogen 3-nitrophthalate,



is obtained when the acid is esterified by the Fischer-Speier method and the product crystallised from carbon disulphide, then from carbon tetrachloride, and finally from benzene until it melts sharply at 95° ; it dissolves readily in alcohol, acetone, benzene, or hot carbon tetrachloride, and both it and the alcohol obtained from it are inactive.

To obtain the active amyl alcohol, the commercial product is treated by Rogers' process, except that hydrogen chloride is employed instead of concentrated hydrochloric acid. By this method, an alcohol having a rotation $\alpha_D -5.95^\circ$ ($l=2$) may be obtained; this is then esterified by the Fischer-Speier method, 1 part of 3-nitrophthalic acid being employed for every 2.5 parts of alcohol and 0.23 part of sulphuric acid. The acid ester is mixed with its own volume of carbon disulphide and the residue then crystallised from benzene until it melts sharply at $113.5-114.5^\circ$. The crystallisation was so conducted that the mother liquor from a fraction of high melting point was employed for the solution of the fraction with the next highest melting point. Active 1-amyl 2-hydrogen 3-nitrophthalate forms well-defined, glistening crystals, fairly readily soluble in most organic solvents, and has $[\alpha]_D +6.5^\circ$ at 17° . The active amyl alcohol obtained on hydrolysis boils at 128° , has a sp. gr. 0.816 at $20^\circ/4^\circ$ and $[\alpha]_D -5.90^\circ$ at 20° ; its odour is quite different from that of ordinary *iso*amyl alcohol. The numerous derivatives of active amyl alcohol described in detail by Guye, Walden, Frankland, and others are in reality mixtures and were mostly obtained from an alcohol containing some 75–80 per cent. of the active constituent.

J. J. S.

Nitrating Action of Nitric Acid on Derivatives of Saturated Hydrocarbons. II. Action of Nitric Acid on Alcohols. By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 48–50).—By gradually adding concentrated nitric acid to an acetic acid solution of dimethylethylcarbinol, diluting with water, and neutralising with excess of potassium hydroxide, the liquid separates into two layers. The alcoholic layer contains the nitro-derivative of the alcohol and a crystalline compound melting at $96-97^\circ$ which is probably the amylene nitrosate, $\text{NO}_3 \cdot \text{CMe}_2 \cdot \text{CMe} \cdot \text{NOH}$, described by Wallach. In the aqueous liquor is found the *oxime* of a hydroxy-ketone having the constitution $\text{OH} \cdot \text{CMe}_2 \cdot \text{CMe} \cdot \text{N} \cdot \text{OH}$, and melting at $82-84^\circ$.

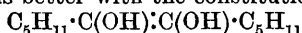
T. H. P.

Syntheses of Tertiary Alcohols of the Fatty Series. By HENRI MASSON (*Compt. rend.*, 1901, 132, 483–485).—By the action of magnesium methyl iodide and magnesium ethyl iodide on alkyl esters in presence of ether, the author has obtained a number of tertiary alcohols of the fatty series, the group $\text{X} \cdot \text{CO}_2\text{Et}$ being converted into $\text{X} \cdot \text{CRR}' \cdot \text{OH}$. He has thus prepared dimethylpropylcarbinol (b. p. 124°), diethylpropylcarbinol (b. p. 159°), *diethyliso*-

butylcarbinol boiling at 172°, *dimethylamylcarbinol* boiling at 162°, *diethylamylcarbinol* boiling at 199°, *dimethylhexylcarbinol* boiling at 178°, and *diethyloctylcarbinol* boiling at 250°. They are all liquids lighter than water, boil without decomposing under normal pressure, and are volatile in steam. When mixed with a little ethyl alcohol, but not otherwise, they yield a precipitate with Denigès' reagent. With iodine and phosphorus, they yield iodo-derivatives, which do not boil without decomposing but are volatile in steam. When these iodo-derivatives are treated with alcoholic potash, they yield olefines, but the best method of obtaining these hydrocarbons is to heat the tertiary alcohols with acetic anhydride; under these conditions, *diethylpropylcarbinol* yields γ -ethyl- β -hexene, $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CEt}\cdot\text{CHMe}$, boiling at 119—120°.

C. H. B.

Action of Esters of Monobasic Fatty Acids on Mixed Organomagnesium Compounds. By VICTOR GRIGNARD (*Compt. rend.*, 1901, 132, 336—338. Compare Abstr., 1900, i, 382).—The first product of the action of magnesium ethyl bromide on ethyl formate appears to be an additive compound, $\text{OEt}\cdot\text{CHEt}\cdot\text{OMgBr}$, which is converted by the further action of the magnesium ethyl bromide into the compound $\text{CHEt}_2\cdot\text{OMgBr}$; the latter is decomposed by water with the formation of *diethylcarbinol*. The action of magnesium *isoamyl* bromide on ethyl formate results in the formation, not, as was expected, of *diisoamylcarbinol*, but of the corresponding *formate*, a colourless liquid of faint, agreeable odour, which boils at 100—101° under 8 mm. pressure. The molecular refraction (59·94—60·171) of this compound accords better with the constitution



than with the normal formula. *Diisoamylcarbinol*, obtained by the hydrolysis of the preceding compound, is a colourless liquid which boils at 105° under 9 mm. pressure. The action of magnesium *isobutyl* bromide on ethyl formate yields a mixture of *diisobutylcarbinol*, which boils at 172—174° under 752 mm. pressure, and the corresponding *formate*, which boils at 173—175° under 750 mm. pressure.

Magnesium methyl iodide reacts with methyl acetate to form *trimethylcarbinol*, whilst magnesium *isoamyl* bromide yields *methyl-diisoamylcarbinol*, which boils at 108—109° under 10 mm. pressure.

N. L.

Methylbutylallylcarbinols containing Normal and Secondary Butyl. By KONSTANTIN TALIEFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 26—35).—*Methylbutylallylcarbinol*, $\text{C}_9\text{H}_{18}\text{O}$, prepared by the action of zinc on methyl butyl ketone (1 mol.) and allyl iodide (1·5 mols.), is a colourless liquid which boils at 179·1°, is insoluble in water, and has a characteristic odour somewhat resembling that of turpentine. It has the sp. gr. 0·84412 at 20°/0° and 0·84497 at 20°/20°, and n_D 1·43990, n_B 1·44857, and n_γ 1·45361. Its *acetyl* derivative, $\text{C}_{11}\text{H}_{20}\text{O}_2$, is a colourless liquid boiling at 196—201° and possessing a pleasant ethereal odour slightly recalling that of turpentine.

Methylsec. butylallylcarbinol, obtained by the action of zinc on methyl *sec.* butyl ketone and allyl iodide, is a colourless liquid boiling at 174·9° and having a faint turpentine-like odour. It is insoluble in

water and has the sp. gr. 0.85438 at 20°/0° and 0.85526 at 20°/20°, n_a 1.44460, n_β 1.45324, and n_γ 1.45850. Its *acetyl* derivative boils at about 190—195°.

When gently oxidised with potassium permanganate solution, both these alcohols yield the corresponding *trihydric alcohols* of the constitution $\text{OH}\cdot\text{CMePr}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, which are obtained as thick syrups readily soluble in water or alcohol, and to a less extent in ether. When more energetically oxidised, the trisubstituted carbinols yield the corresponding *methylbutylhydracrylic acids*, $\text{C}_8\text{H}_{16}\text{O}_3$, in the form of thick syrups; the *calcium, barium, zinc and silver* salts of both acids were prepared. T. H. P.

New Diprimary Glycol. *αδ-Butanediol* or *Tetramethylene Glycol* and its *Diacetin*. By JULES HAMONET (*Compt. rend.*, 1901, 132, 631—633).—The *diacetin*, $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OAc}$, obtained by treating *αδ*-diiodobutane with a mixture of silver acetate and acetic acid, crystallises in large, arborescent needles melting at 12° and boiling at 124° and 230°, under pressures of 20 and 751 mm. respectively; it has a sp. gr. 1.048 at 20°. *αδ-Butanediol*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, obtained by the hydrolysis of the preceding compound, is a viscous, colourless liquid, miscible in all proportions with water, has a sp. gr. 1.020 at 20° and boils at 230° under 759 mm. pressure; when cooled to 0°, it is slowly converted into crystals melting at 16°. It does not dissolve cupric hydroxide in presence of alkalis, and is easily separated from water by addition of potassium carbonate. N. L.

Pentahydric Alcohol from Propyldiallylcarbinol. By DMITRI MARKO (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 36—38).—By the action of potassium permanganate on propyldiallylcarbinol, an *alcohol* of the constitution $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{C}(\text{OH})[\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}]_2$ is obtained. Its *penta-acetyl* derivative was prepared. T. H. P.

Action of Zinc Powder on Saturated Fatty Acids. By ALEXANDRE HÉBERT (*Compt. rend.*, 1901, 132, 633—635).—When commercial stearic acid is distilled with dry zinc powder at 350—400°, carbon dioxide, hydrogen, and gaseous hydrocarbons, chiefly unsaturated, are evolved, whilst the distillate consists of a little water and about 70 per cent. of a mixture of liquid and solid hydrocarbons of the ethylene series, ranging from $\text{C}_{17}\text{H}_{34}$ to $\text{C}_{90}\text{H}_{180}$. This mixture has been submitted to fractional distillation, and the various fractions analysed, and their bromine additive products examined. N. L.

Preparation of Methyl Acrylate. By OTTO RÖHM (*Ber.*, 1901, 34, 573—574).—An 80 per cent. yield of dibromopropyl alcohol may be obtained by the addition of bromine to allyl alcohol; this is then oxidised by Biilmann's method (*J. pr. Chem.*, 1900, [ii], 61, 216), esterified by Caspary and Tollens' process (*Annalen*, 1872, 167, 247), and treated with zinc. A 77 per cent. yield of methyl acrylate is obtained when the dibromo-ester (550 grams) is gradually run into a mixture of zinc foil (200 grams) and methyl alcohol (200 grams) contained in a reflux apparatus. J. J. S.

Conversion of Dimethylacrylic Acid into Dimethylpyruvic Acid. By LOUIS BOUVEAULT and A. WAHL (*Compt. rend.*, 1901, 132, 416—418. Compare this vol., i, 4 and 114).—*Ethyl dimethylpyruvate*, $\text{CHMe}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, produced by heating at 100° the hydrochloric acid solution of ethyl α -aminodimethylacrylate, is a liquid boiling at 65 — 69° under 15 mm. pressure, and of sp. gr. 1.031 at $0^\circ/0^\circ$. The *oxime* forms colourless needles melting at 55° ; it is very soluble in all neutral solvents except water and light petroleum. The *semicarbazone* separates from a mixture of ether and light petroleum in the form of colourless prisms and melts at 95 — 96° .

Dimethylpyruvic acid, obtained by heating its ethyl salt with water at 140 — 150° , melts at 31° , and boils at 65 — 67° under 10 mm. pressure; it is very soluble in water, alcohol, or ether. The *oxime* crystallises from ether in white leaflets and melts at 163 — 165° ; the *phenylhydrazone* crystallises from alcohol in yellow needles and melts at 156 — 157° .

G. T. M.

Distillation of Castor Oil. By HERMANN THOMS and GEORG FENDLER (*Arch. Pharm.*, 1901, 239, 1—6).—When castor oil is distilled, undecenoic acid and heptaldehyde are obtained, the thermometer rising to about 280° . When about half of the oil has passed over, the residue suddenly swells up, forming a substance like indiarubber in consistency. This was washed with alcohol, chloroform, and ether in succession, and was then found to have the composition $\text{C}_{33}\text{H}_{58}\text{O}_5$, corresponding to the *anhydride* of *triundecenoic acid*. It was hydrolysed with alcoholic potash; the product was found to yield a *hexadecenoic acid*, $\text{C}_{16}\text{H}_{30}\text{O}_2$, melting at 36° , when fused with potassium hydroxide; sebacic acid and an *acid*, $\text{C}_{18}\text{H}_{34}\text{O}_4$, when oxidised with fuming nitric acid; and sebacic and lower fatty acids when oxidised with permanganate. If the distillation of the castor oil is stopped just before the swelling up would otherwise take place, the oily residue yields glycerol, when hydrolysed with alcoholic potash, and the same product as was obtained by hydrolysing the solid residue. This oily residue has the composition $\text{C}_{105}\text{H}_{184}\text{O}_{18}$, corresponding to the *glyceride* of triundecenoic acid; when it swells up on heating, the presumption is that it decomposes into water, acraldehyde, and triundecenoic anhydride.

C. F. B.

New Reactions of Organometallic Derivatives. Alkyl Esters of α -Alkyl- β -ketonic Acids. By EDMOND E. BLAISE (*Compt. rend.*, 1901, 132, 478—480).—The alkyl esters of the α -alkyl- β -ketonic acids are obtained by condensing nitriles with the alkyl esters of the α -bromoacetic acids in presence of zinc. The reaction takes place readily with the α -cyclic nitriles, benzonitriles, and cyclic *p*-nitriles, but not with cyclic *o*-nitriles. Cyclic nitriles in which the nitrogen is attached to a side chain, as in benzyl cyanide, readily undergo the condensation. The method is general, and the yield varies from 25 to 50 per cent. The salts are readily converted into ketones by treatment with boiling aqueous solutions of alkali hydroxides.

Ethyl propionylisopropylacetate, $\text{CH}_3\text{Me}\cdot\text{CO}\cdot\text{CHPr}\cdot\text{CO}_2\text{Et}$, from ethyl bromoisovalerate and propionitrile, boils at 108 — 109° under 21 mm. pressure. *Ethyl butyrylisobutyrate*, $\text{CH}_3\text{Me}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, from ethyl bromoisobutyrate and butyronitrile, boils at 108 — 110° under

29 mm. pressure. The corresponding *propyl isopropyl ketone* boils at 129—130°, and its *semicarbazone* melts at 117—118°. *Ethyl isohexoyl-isobutyrate*, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$, from ethyl bromoisobutyrate and isohexonitrile, boils at 121—124° under 20—22 mm. pressure and yields *isopropyl isoamyl ketone* which boils at 171—172°, whilst its *semicarbazone* melts at 98—99°. *Ethyl p-toluoylisobutyrate*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$, from *p*-toluonitrile and ethyl bromoisobutyrate, boils at 169—172° under 25 mm. pressure. *Ethyl phenacetyl-isobutyrate*, $\text{CH}_2\text{Ph} \cdot \text{CO} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$, from benzyl cyanide and ethyl isobutyrate, boils at 164—165° under 16 mm. pressure, and solidifies when cooled. The corresponding *benzyl isopropyl ketone* boils at 234—235°, and its *semicarbazone* melts at 140—141°. C. H. B.

Resolution of Trimethylsuccinic Acid into its Optical Antipodes. By VINCENZO PAOLINI (*Gazzetta*, 1900, 30, ii, 506—510).—On adding boiling aqueous trimethylsuccinic acid to an alcoholic solution of quinine and cooling the liquid, the salt of the dextro-modification of the acid separates out in radiating, white, silky needles, whilst quinine *l*-trimethylsuccinate can be recovered from the mother liquors.

Quinine d-trimethylsuccinate, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot \text{C}_7\text{H}_{12}\text{O}_4$, melts at 198°. *d-Trimethylsuccinic acid*, when crystallised from water, melts at 140° and has $[\alpha]_D + 4.83^\circ$. With acetyl chloride and a benzene solution of aniline, it yields laevorotatory *anil-d-trimethylsuccinic acid*, $\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}$, which separates from dilute alcohol in white, feathery needles melting at 130—135° and insoluble in sodium hydroxide solution.

Quinine l-trimethylsuccinate crystallises from dilute alcohol in white, radiating, silky needles melting at 188°. *l-Trimethylsuccinic acid* melts at 140° and has $[\alpha]_D - 1.31^\circ$. *Anil-l-trimethylsuccinic acid* melts at about 140° and is dextrorotatory. T. H. P.

Polymerisation of Unsaturated Acids. III. α -Methylene-glutaric Acid, a Product of the Polymerisation of Acrylic Acid. By HANS VON PECHMANN and OTTO RÖHM (*Ber.*, 1901, 34, 427—429).—When methyl acrylate, dissolved in anhydrous ether, is treated with sodium methoxide, it is polymerised to an oil which, when hydrolysed with dilute hydrochloric acid, yields *α -methylene-glutaric acid*, $\text{CO}_2\text{H} \cdot \text{C}(\text{CH}_2) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, as a voluminous crystalline powder; this softens at 125—126°, melts at 129—130°, and forms a *hydrobromide* which melts at 112° and, when reduced with sodium amalgam, yields *α -methylglutaric acid*. R. H. P.

A New Trimethylenedicarboxylic Acid. By VINCENZO PAOLINI (*Gazzetta*, 1900, 30, ii, 497—505).—By the action of phosphorus pentachloride on ethyl trimethylhydroxysuccinate, Komppa (*Abstr.*, 1896, i, 597) obtained ethyl chlorotrimethylsuccinate. By carrying out the reaction in chloroform solution and heating the mixture on the water-bath until the evolution of hydrogen chloride ceases, the author obtained a liquid boiling at 110—115° under 15 mm. pressure, which proves to be *ethyl dimethyltrimethylenedicarboxylate*.

Dimethyltrimethylenedicarboxylic acid, $\text{CH}_2 \begin{array}{c} \text{CMe} \cdot \text{CO}_2\text{H} \\ | \\ \text{CMe} \cdot \text{CO}_2\text{H} \end{array}$, separates from water in aggregates of prismatic crystals melting at 153—154°.

It is stable towards permanganate and does not take up bromine. The *calcium* salt, with $1\text{H}_2\text{O}$, was analysed.

Acetyl chloride converts the acid into its anhydride, which was not separated but was directly converted into the *anilide* of the acid, $\text{CO}_2\text{H}\cdot\text{C}_3\text{H}_2\text{Me}_2\cdot\text{CO}\cdot\text{NHPh}$, separating from alcohol in feathery, white needles melting at 157° . When heated at about 170° , the latter gives up water and yields the corresponding *anil* acid, $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}$, which separates from dilute alcohol in white, silky needles melting at 105° .

T. H. P.

Formaldehyde. By CARL D. HARRIES (*Ber.*, 1901, 34, 635—637).—Solid formaldehyde can readily be obtained by distilling pure para-formaldehyde and condensing the vapour in liquid air. The melting point, determined with a toluene thermometer, was found to be about -92° .

T. M. L.

Formation and Decomposition of Acetals. By MARCEL DELÉPINE (*Compt. rend.*, 1901, 132, 331—334. Compare this vol., i, 3, and ii, 6).—The formation of acetals is a limited reaction and the laws regulating the production and decomposition of these compounds are similar to those observed in the analogous cases of esterification and hydrolysis. In this connection, the behaviour of methylal, the formals of ethyl and propyl alcohols, the formals of glycol, erythritol, and mannitol, and the acetal of mannitol has been studied. In each case, the same final limit is reached whether the starting point is the system, alcohol-aldehyde or formal-water. The limiting proportion of formal or acetal produced is decreased by the presence of water, but increased by the use of an excess of either alcohol or aldehyde (more especially of the former), by rise in temperature, and by addition of acids. Acids are peculiarly efficacious in facilitating the reaction, and are, perhaps, necessary for decomposition. The nature of the acid and its concentration, if the latter is not too great, are without influence on the result. The decomposition and formation of systems reacting in presence of hydrochloric acid may be represented as a function of the time by the usual logarithmic curves.

N. L.

Condensation of isoValeraldehyde with Acetaldehyde. By ALFRED WÖGRINZ (*Monatsh.*, 1901, 22, 1—13).—This condensation is best effected by the use of a saturated solution of potassium carbonate. The *aldol*, $\text{C}_7\text{H}_{14}\text{O}_2$, which is formed is a colourless liquid and distils at $100\text{--}110^\circ$ under 25 mm. pressure; when freshly distilled, it is unimolecular, but when kept, polymerises into a viscous bimolecular modification. The *oxime* boils at 144° under 25 mm. pressure. Oxidation produces, together with other acids, a viscid, liquid *hydroxy-acid*, $\text{C}_7\text{H}_{14}\text{O}_3$. By long heating, the aldol passes into an *unsaturated aldehyde*, $\text{C}_7\text{H}_{12}\text{O}$, which boils at $149\text{--}150^\circ$ under atmospheric pressure, and on oxidation yields *isovaleric*, *acetic*, *oxalic*, and an unknown acid.

K. J. P. O.

Condensation of isoButaldehyde with Crotonaldehyde. By RICHARD PLATTENSTEINER (*Monatsh.*, 1901, 22, 14—20).—By condensation of *isobutaldehyde* with crotonaldehyde by aid of a 20 per

cent. solution of potassium carbonate, an *aldol*, $C_8H_{14}O_2$, was obtained as a yellow oil which decomposed at 80° and could not be distilled. The *oxime*, $C_8H_{15}O_2N$, is an oil. Reduction with aluminium amalgam converts the aldol into a *dihydric alcohol*, $C_8H_{16}O_2$, a dark yellow oil boiling at 127 — 134° under 18 mm. pressure; the *diacetate*, $C_8H_{14}O_2Ac_2$, boils at 127 — 132° under 15 mm. pressure, and forms a dibromo-additive product. The dihydric alcohol is also obtained by the action of alcoholic potassium hydroxide on a mixture of *isobutaldehyde* and *crotonaldehyde*.
K. J. P. O.

Condensation of *iso*Butaldehyde with Propaldehyde. By MORIZ KOHN (*Monatsh.*, 1901, 22, 21—58).—By the action of a saturated solution of potassium carbonate, the aldehydes are condensed to the *aldol*, $CHMe_2 \cdot CH(OH) \cdot CHMe \cdot CHO$, a colourless, oily liquid, boiling at 98 — 100° under 20 mm. pressure. The *oxime*, $C_7H_{15}O_2N$, a colourless thick oil, boils at 144° under 21 mm. pressure. On oxidation, propionic acid and β -hydroxy- α -dimethylvaleric acid are obtained, the latter of which melts at 97° . Reduction with aluminium amalgam produces a *heptylene glycol*, $CHMe_2 \cdot CH(OH) \cdot CHMe \cdot CH_2 \cdot OH$, which crystallises in aggregates of needles, melts at 58 — 59° , and boils at 117 — 118° and 215 — 216° under pressures of 17 and 740 mm. respectively; the *diacetate*, $C_7H_{14}O_2Ac_2$, boils at 116 — 117° and 226 — 227° under pressures of 18 and 748 mm. respectively.

On heating the aldol with a saturated solution of sodium acetate, a *hepteno-aldehyde*, $CHMe_2 \cdot CH : CMe \cdot CHO$, is formed; it is best prepared by the action of dilute aqueous sodium hydroxide on a mixture of *isobutaldehyde* and propaldehyde. It boils at 146 — 148° , oxidises in the air, and absorbs bromine. The *oxime*, $C_7H_{13}ON$, boils at 100° under 17 mm. pressure, and when heated with acetic anhydride is converted into an *acetate*, $C_7H_{12}ONAc$, boiling at 122° under 17 mm. pressure. When heated at 180° with acetic anhydride, the oxime yields a *hepteno-nitrile*, $C_7H_{11}N$, a colourless, mobile oil, which boils at 62 — 64° under 18 mm., and 162 — 164° under atmospheric pressure. On hydrolysis of the latter by sulphuric acid or potassium hydroxide, α -dimethyl- α -butenoic acid (Abstr., 1899, i, 331) is formed. This same acid is formed by atmospheric oxidation of the unsaturated aldehyde, and on more vigorous oxidation is converted into *isobutyric* and acetic acids.
K. J. P. O.

Acetaldol [Aldol]. By JAKOB H. HALPERN (*Monatsh.*, 1901, 22, 59—65).—The condensation of acetaldehyde to aldol can be effected by means of dry potassium or sodium carbonate, and of aqueous solutions of sodium carbonate or sodium acetate, but not by calcium hydroxide, alcoholic potassium hydroxide, or lead monoxide. The method preferred is that of Orndorff and Newbury (Abstr., 1892, 1423), in which aqueous potassium carbonate is used. Aluminium amalgam reduces aldol or paralldol to butylene glycol. Freshly distilled aldol is unimolecular, whilst its polymerides, the viscid variety and paralldol, are bimolecular.
K. J. P. O.

Action of Hydrazine Hydrate on α -Methyl- β -ethylacraldehyde. By FRITZ DEMMER (*Monatsh.*, 1901, 22, 69—76).—When

α -methyl- β -ethylacraldehyde is warmed on the water-bath with hydrazine hydrate, an *aldazine*, $C_{12}H_{20}N_2$, is formed, which crystallises in pale yellow needles, melts at $54-55^\circ$, and boils at 150° under 20 mm. pressure. It unites with 4 atoms of bromine, and is hydrolysed by hydrochloric acid into its constituents. On reduction, ammonia is produced.

K. J. P. O.

Action of Potassium Hydroxide on β -Hydroxy- $\alpha\alpha$ -dimethylpropaldehyde (An Analogue of Cannizzaro's Reaction in the Aliphatic Series). By LEO WESSELY (*Monatsh.*, 1901, 22, 66—68. Compare Abstr., 1900, i, 428).—The formula of this hydroxyaldehyde shows analogies with that of benzaldehyde, as the $\cdot CHO$ group is combined with a carbon atom to which no hydrogen is attached. In addition, similarity is exhibited in certain physical constants, and in the reaction with potassium hydroxide, which is expressed by the equation, $2OH\cdot CH_2\cdot CMe_2\cdot CHO + KOH = OH\cdot CH_2\cdot CMe_2\cdot CH_2\cdot OH + OH\cdot CH_2\cdot CMe_2\cdot CO_2K$. The yields of pentaglycol ($\alpha\gamma$ -dihydroxy- $\beta\beta$ -dimethylpropane) and the hydroxy-acid (hydroxypivalic acid) are nearly quantitative.

K. J. P. O.

Synthesis of Methylheptenone. By WLADIMIR IPATIEFF (*Ber.*, 1901, 34, 594—596. Compare Tiemann and Semmler, Abstr., 1895, i, 646; Barbier and Bouveault, 1896, i, 55, 637; Verley, 1898, i, 557).—A fairly good yield of *ethyl $\delta\delta$ -dimethylallylacetate*, $CMe_2\cdot CH\cdot CH_2\cdot CHAc\cdot CO_2Et$, may be obtained by the condensation of ethyl sodioacetate and $\alpha\gamma$ -dibromo- γ -methylbutane. It is a colourless liquid, distilling at $120-122^\circ$ under 11—12 mm. pressure, and when boiled with baryta water or dilute alcoholic potash yields methylheptenone identical in all properties with the product obtained from natural sources.

J. J. S.

Constitution of Dextrose. By L. J. SIMON (*Compt. rend.*, 1901, 132, 487—490).—The author considers that the isomerism of the pentacetates, phenylhydrazones, chloraloses, and glucosides derived from dextroses, and the α - and γ -modifications of the dextroses themselves, is not of the same order as the isomerism between the different hexoses, since all the former are readily reconverted into the parent substance without yielding any other hexose. In all cases, the rotatory power of the β -dextroses is intermediate between, and approximates to the mean of, the rotatory powers of the α - and γ -modifications, and this is true also of the methylglucosides of Fischer. The author explains these facts by assuming that dextrose is tautomeric, the β -modification having the constitution represented by the ordinary aldehydic formula, whilst the α - and γ -modifications, which show mutarotation, correspond with the two stereochemical configurations of molecules of the constitution $OH\cdot CH_2\cdot CH(OH)\cdot \underset{\underset{O}{|}}{CH}\cdot CH(OH)\cdot CH(OH)\cdot \underset{\underset{O}{|}}{CH}\cdot OH$,

containing an additional asymmetric carbon atom. From this point of view, the hydrazones, oximes, &c., correspond with the α - and γ -modifications, but since modifications may also exist with the aldehydic constitution, these compounds may be expected to show mutarotation.

C. H. B.

The Phenylhydrazones of Dextrose and their Mutarotation.

By L. J. SIMON and H. BÉNARD (*Compt. rend.*, 1901, 132, 564—566).—The mutarotation of Skraup's phenylhydrazone of *d*-dextrose may be expressed by the exponential equation, $[\alpha]_D^{20} = -52.9^\circ + 53.67e^{-0.0044133t}$, where t is time expressed in minutes. This expression indicates that, initially, the substance should be slightly dextrorotatory; the first reading in aqueous solution gave $[\alpha]_D$ as -6.84° , after 24 hours the optical activity reached its maximum, and the final observation gave a rotation of -52.9° . When the substance is dissolved in alcohol, the optical activity remains constant for several hours, $[\alpha]_D$ being -8° ; after 6 hours, the rotation increases and the limiting value -22.5° is reached after 36 hours. The presence of potassium hydroxide or dilute hydrochloric acid accelerates the change of rotation without affecting the final value, the acceleration being greater in the case of the acid; the hydrazone becomes, however, partially hydrolysed in moderately concentrated acid solution. Fischer obtained a *d*-dextrose phenylhydrazone melting at 115 — 116° , whereas Skraup's compound melts at 144° (Abstr., 1887, 567). The authors were not able to obtain Fischer's hydrazone in a state of purity, their preparations always containing a certain amount of the isomeride.

A 4 per cent. solution of a specimen melting at 125° gave, after 25 minutes, a rotation -66.57° ; the optical activity then decreased regularly until, after 36 hours, its limiting value was reached and found to be identical with that of Skraup's isomeride. The results are in accordance with those observed by Tanret in studying the rotation of the α - and γ -modifications of dextrose (compare Abstr., 1895, i, 490).
G. T. M.

Isomeric Acetyl Halogen Derivatives of Dextrose.

By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Sitzungsber. Akad. Wiss. Berlin*, 1901, 13, 316—322. Compare Abstr., 1894, i, 3).—The isomeric pentacetyldextroses, when treated with dry hydrogen chloride or bromide in the liquid form, yield the corresponding acetylchloro- or acetylbromo-dextroses. β -Tetracetylchlorodextrose, obtained from the pentacetyldextrose melting at 134° , crystallises from light petroleum in aggregates of colourless needles and melts at 73 — 74° ; the yield is almost quantitative. The compound is converted into tetracetyl- β -methylglucoside by the action of finely divided silver carbonate suspended in methyl alcohol; the reaction, however, takes place more slowly than in the case of the corresponding bromo-derivative. The chloro-derivative may be prepared without the use of liquid hydrogen chloride by saturating with the gas a solution of pentacetyldextrose in acetic anhydride at -20° , and then heating the mixture in sealed tubes at 45° . β -Tetracetylbromodextrose, obtained by the use of liquid hydrogen bromide, is identical with the compound prepared by Königs and Knorr (Abstr., 1889, 952).

α -Tetracetylchlorodextrose obtained from the pentacetyldextrose melting at 112° , crystallises from light petroleum in colourless needles and melts at 63° .

Tetracetyl- α -methylglucoside, produced by treating the preceding compound with silver carbonate, crystallises from water in lustrous prisms

and melts at 100—101°; this substance yields α -methylglucoside on boiling with baryta water.

α -Tetracetyl bromodextrose crystallises in colourless prisms and melts at 79—80°. It is less stable than its chlorine analogue and slowly decomposes on keeping.

Tetracetyl chlorogalactose, prepared from the pentacetyl galactose melting at 142°, crystallises in spherical aggregates of prisms, and melts at 74—75° (compare Abstr., 1889, 1131). G. T. M.

Carbamide Derivatives of Sugars. By N. SCHOORL (*Proc. K. Akad. Wetensch., Amsterdam*, 1901, 3, 459—462).—*Dextrose-ureide*, $C_6H_{12}O_5 \cdot N \cdot CO \cdot NH_2$, obtained by heating dextrose (1 mol.) and carbamide (2 mols.) with 5 per cent. sulphuric acid at 50° for 20 days, melts at 206°, has $[\alpha]_D - 23^\circ$ at 15° (in 1 per cent. aqueous solution) and is hydrolysed by dilute acids.

Dextrosephenylureide, obtained in a similar manner from dextrose and phenylcarbamide, melts at 223° and has $[\alpha]_D - 55^\circ$ (in 1 per cent. solution). Lactose, galactose, mannose, arabinose, and xylose also condense with carbamide. Since methyl-, phenyl-, benzyl-, thio- and phenylthio-carbamides all condense with dextrose, whilst *sym*-disubstituted carbamides do not, it appears that these ureides have a constitution similar to that of oximes and phenylhydrazones. R. H. P.

Synthetic Action of Yeast Maltase. By OSKAR EMMERLING (*Ber.*, 1901, 34, 600—605).—On repeating Hill's experiments (*Trans.*, 1898, 73, 634) as to the action of yeast maltase on pure dextrose, the author finds that not maltose but *isomaltose* is the disaccharide formed; the action of the enzyme on maltose is therefore not truly reversible as considered by Hill, but is similar in character to that of the mineral acids, which are capable of converting dextrose into *isomaltose* (Fischer, Abstr., 1891, 412; 1896, i, 119). The osazone isolated by Hill melting at 178—180° was probably a mixture of glucosazone and *isomaltosazone*, not *maltosazone* which melts at 206°. In the author's experiments, the *isomaltose* was isolated in the form of its osazone (m. p. 149—152°) after destroying the excess of dextrose by fermentation with a pure yeast incapable of affecting maltose. The yield was in all cases small. W. A. D.

Constitution of Gentianose. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1901, 132, 571—574. Compare Abstr., 1898, i, 597).—Gentianose, $C_{18}H_{32}O_{16}$, a sugar extracted from the fresh gentian root, is a hexotriose hydrolysed by the action of invertase or very dilute sulphuric acid (0.2 per cent.) into a new hexobiose *gentiobiose*, $C_{12}H_{22}O_{11}$, and *lævulose*; more concentrated acid or the fermenting extract of *Aspergillus niger* hydrolyses it completely into 1 mol. of *lævulose* and 2 of dextrose. Gentiobiose has not yet been obtained crystalline, but it is nevertheless a definite compound resembling maltose; its osazone is soluble in hot water, crystallises on cooling the solution, and melts at 142°; it is feebly dextrorotatory $[\alpha]_D$ being 7.7°. In cupric-reducing power, 0.083 gram of the new sugar is equivalent to 0.05 gram of invert sugar. When treated in the cold

with an extract of *Aspergillus*, or when heated to 110° with 3 per cent. sulphuric acid, gentiobiose is hydrolysed into 2 mols. of dextrose.

G. T. M.

Regularities in the Melting Points of Aliphatic Diamines. By FELIX KAUFLEDER (*Chem. Zeit.*, 1901, 25, 133).—It is pointed out that in the homologous series of aliphatic diamines with the amino-groups at the ends of the chain, the compounds with an odd number of carbon atoms have relatively lower melting points than those with an even number of carbon atoms, thus:—Ethylenediamine, $+8.5^{\circ}$; trimethylenediamine, liquid; tetramethylenediamine, 27° ; pentamethylenediamine, liquid; hexamethylenediamine, 40° ; octomethylenediamine, 51° ; nonomethylenediamine, 37° ; decamethylenediamine, 61° .

J. J. S.

isoPropanolamine [β -Aminoisopropyl Alcohol]. By EDGAR PEETERS (*Bull. Acad. Roy. Belg.*, 1901, 9—16).—The author has reduced β -nitroisopropyl alcohol (Abstr., 1895, i, 638), best with tin and hydrochloric acid, to β -aminoisopropyl alcohol, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$. This substance boils at 160 — 171° under 750 mm. pressure, has a sp. gr. 0.973 and n_D 1.45 at 18° ; its molecular weight, determined cryoscopically in acetic acid solution, is normal; its vapour density, however, as determined by Hofmann's method under pressures of 120—180 mm., decreases from 0.7 to 0.5 of the normal as the temperature rises from 100 to 185° , whilst as determined by V. Meyer's method at 185° , it is 1.45 times the normal value. The base forms a *platinichloride* and a *picrate* melting at 195° and 142° respectively; also a *dibenzoate* melting at 87° .

C. F. B.

Alcohol Bases. By HERMANN MATTHES (*Annalen*, 1901, 315, 104—137). Compare Abstr., 1898, i, 399).—The *picrolonates* of methylhydroxyethylamine and ethylhydroxyethylamine melt and decompose at 239° and 245° respectively.

Hydroxyethylpropylamine, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHPr}^a$, prepared from propylamine and ethylene oxide, is a colourless oil which quickly absorbs water and carbon dioxide; it boils at 182° under 746 mm. pressure, has a sp. gr. 0.9005 at $20^{\circ}/4^{\circ}$, and n_D 1.4428 at 20° . The *hydrochloride* is hygroscopic, the *platinichloride* is an oil, and the *aurichloride* melts at 85° , whilst the *picrate* and *picrolonate* melt at 104 — 106° and 238° respectively.

Hydroxyethylbutylamine, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_4\text{H}_9$, boils at 199 — 200° under 756 mm. pressure, has a sp. gr. 0.8907 at $20^{\circ}/4^{\circ}$, and n_D 1.4437 at 20° . The *hydrochloride* is excessively hygroscopic, whilst the *picrate* and *picrolonate* melt at 98° and 218° respectively.

Hydroxyethylhexylamine, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_{13}$, boils at 231° under 747 mm. pressure, has a sp. gr. 0.8829 at $20^{\circ}/4^{\circ}$, and n_D 1.4472 at 20° . The *hydrochloride*, *aurichloride*, and *platinichloride* are deliquescent, whilst the *picrate* crystallises in pale yellow prisms melting at about 80° ; the *picrolonate* melts and decomposes at 208 — 210° .

Hydroxyethylheptylamine, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_7\text{H}_{15}$, melts at about 35° , and boils at 250 — 253° under 751 mm. pressure; it has a sp. gr. 0.8819 at $20^{\circ}/4^{\circ}$, and n_D 1.4510 at 20° . The *hydrochloride*, *aurichloride*,

and *platinichloride* are hygroscopic, whilst the *picrate* and *picrofonate* melt at 70—71° and 196° respectively.

Hydroxyethylisopropylamine, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHPr}^\beta$, boils at 171° under 741 mm. pressure, has a sp. gr. 0.8970 at 20°/4°, and n_D 1.4395 at 20°. The *hydrochloride*, *aurichloride*, and *platinichloride* are hygroscopic, and the last-named melts at about 85°; the *picrate* and *picrofonate* melt at 129° and 228° respectively.

Hydroxyethylisobutylamine, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\text{Pr}^\beta$, boils at 190° under 756 mm. pressure, has a sp. gr. 0.8818 at 20°/4°, and n_D 1.4402 at 20°; the *picrate* and *picrofonate* melt at 115—117° and 232° respectively.

Hydroxyethylisoamylamine, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr}^\beta$, boils at 209—210° under 751 mm. pressure, has a specific gravity 0.8822 at 20°/4°, and n_D 1.4447 at 20°; the *hydrochloride* is exceedingly hygroscopic, whilst the *picrate* and *picrofonate* melt at 94—95° and 220° respectively.

Dihydroxydiethylamine, *methylidihydroxydiethylamine*, and *ethylidihydroxydiethylamine* have been already described (*loc. cit.*); the *picrofonate* of methylidihydroxydiethylamine crystallises from alcohol in lustrous, brownish-yellow prisms and melts at 164°.

Dihydroxydiethylpropylamine, $\text{NPr}^\alpha(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$, boils at 202—204° and 262—264° under 150 mm. and 753 mm. pressure respectively; it has a sp. gr. 0.9854 at 20°/4°, and n_D 1.4624 at 20°. The *picrate* and *picrofonate* melt at 85—90° and 126—128° respectively.

Dihydroxydiethylbutylamine, $\text{C}_4\text{H}_9\cdot\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$, boils at 214° and 273—275° under 150 mm. and 741 mm. pressure respectively; it has a sp. gr. 0.9681 at 20°/4°, and n_D 1.4620 at 20°. The *picrate* and *picrofonate* melt at 88—95° and 135—136° respectively.

Dihydroxydiethylhexylamine, $\text{C}_6\text{H}_{13}\cdot\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$, boils at 230—235° and 295—300° under 150 mm. and 751 mm. pressure respectively; it has a sp. gr. 0.9472 at 20°/4°, and n_D 1.4630 at 20°. The *picrofonate* melts at about 98°.

Dihydroxydiethylheptylamine, $\text{C}_7\text{H}_{15}\cdot\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$, boils at 240—250° and 310—320° under 150 mm. and 751 mm. pressure respectively; it has a sp. gr. 0.9301 at 20°/4°, and n_D 1.4620.

Dihydroxydiethylisopropylamine, $\text{NPr}^\beta(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$, boils at 200° and 261° under 150 mm. and 741 mm. pressure respectively; it has a sp. gr. 0.9859 at 20°/4°, and n_D 1.4620 at 20°. The *picrate* and *picrofonate* melt at 145° and 125° respectively.

Dihydroxydiethylisobutylamine, $\text{C}_4\text{H}_9\cdot\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$, boils at 202—204° and 264—265° under 150 mm. and 742 mm. pressure respectively; it has a sp. gr. 0.9534 at 20°/4°, and n_D 1.4561. The *picrofonate* melts at 113—114°.

Dihydroxydiethylisoamylamine, $\text{C}_5\text{H}_{11}\cdot\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$, boils at 216—219° and 278—281° under 150 mm. and 749 mm. pressure respectively; it has a sp. gr. 0.9516 at 20°/4°, and n_D 1.4598 at 20°. The *picrofonate* melts at 120—123°.

M. O. F.

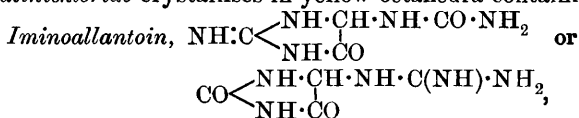
Alkylcyanomalonic Esters and their Corresponding Alkylcyanoacetic Acids. By ALBIN HALLER and GEORGES BLANC (*Compt. rend.*, 1901, 132, 381—384. Compare Abstr., 1882, 1280).—The silver derivative of ethyl cyanomalonate, produced by treating

the corresponding sodium compound with an aqueous solution of silver nitrate, reacts in its ketonic form when mixed with alkyl iodides dissolved in dry ether, giving rise to the corresponding cyanoalkylmalonic esters. The *ethyl* esters of cyanomethylmalonic, cyanoethylmalonic, and cyano-*n*-propylmalonic acids are mobile liquids having a faint odour and neutral reaction; they boil at 135°, 142—145°, and 155—157° respectively under pressures of 28—30 mm. When treated with boiling concentrated hydrochloric acid for 24 hours, these compounds are completely hydrolysed, with the formation of ammonium chloride, carbon dioxide, and the respective monocarboxylic derivatives, namely, propionic, butyric, and *n*-valeric acids. The addition of excess of 30 per cent. potassium hydroxide to these ethers brings about a vigorous reaction resulting in the formation of the corresponding cyanomonocarboxylic acids. These products were characterised by conversion into their calcium salts, and also by the formation of their anilides by the phenyl-carbimide method (compare Abstr., 1896, i, 32). The anilides are sparingly soluble in water or light petroleum, but readily dissolve in alcohol.

α-Cyanopropionanilide, $\text{CN}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NHPh}$, *α*-cyanobutyroanilide, $\text{CN}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{NHPh}$, and *α*-cyanovaleranilide, $\text{CN}\cdot\text{CHPr}^a\cdot\text{CO}\cdot\text{NHPh}$, melt at 104—105°, 86—87°, and 88—89° respectively. G. T. M.

Compounds of Glyoxylic Acid with Guanidine and Amino-guanidine. By OSCAR DOEBNER and SIMON GÄRTNER (*Annalen*, 1901, 315, 1—8).—Although glyoxylic acid unites with carbamide (2 mols.) to form allantoin, combination with guanidine proceeds on different lines. In a cold, aqueous solution, the guanidide of glyoxylic acid is produced, whilst at 100° ammonia is eliminated, and iminoallantoin is formed.

Guanidineglyoxylic acid, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, prepared by adding guanidine carbonate to a 50 per cent. aqueous solution of glyoxylic acid until carbon dioxide is no longer liberated, crystallises from water in slender, colourless needles containing $\frac{1}{2}\text{H}_2\text{O}$, and melts at 210° to a brown liquid which evolves gas. The *ammonium* salt begins to turn brown at 198°, and melts, decomposing, at 225°. The *platinichloride* crystallises in yellow octahedra containing $1\text{H}_2\text{O}$.



obtained on adding guanidine carbonate (2 mols.) to a 15 per cent. solution of glyoxylic acid, and heating in a reflux apparatus during 20 minutes, crystallises from hot water, and sublimes at about 300° without undergoing fusion; the crystals contain $1\text{H}_2\text{O}$, which is removed at 130—140°. The *platinichloride* forms rhombic crystals containing $2\text{H}_2\text{O}$, and the *mercurichloride* crystallises in small white needles; the *aureichloride* is readily soluble in hot water, and crystallises in long, yellow prisms containing $2\text{H}_2\text{O}$.

Aminoguanidineglyoxylic acid, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, produced from aminoguanidine acetate and glyoxylic acid, crystallises

from hot water in aggregates of needles, and melts at 161° , when it decomposes.
M. O. F.

Potassium and Sodium Thiocyanates and a Blue Colour produced by Heating Them. By WILLIAM B. GILES (*Chem. News*, 1901, 83, 61—62).—When potassium thiocyanate or cyanide containing some, but not too much, sulphur, and no carbonate, is heated, a blue colour forms at a dull red heat, disappears on cooling, but reforms on reheating.
D. A. L.

Presence of Guanine in Commercial Uric Acid. By LOUIS HUGOUNENQ (*J. Pharm.*, 1901, [vi], 13, 167—169).—Commercial uric acid always contains guanine, which can be partly, but not entirely, removed by extraction with boiling dilute hydrochloric acid. The guanine may also be isolated by treatment of the commercial acid with an alkaline persulphate, whereby the uric acid is oxidised, while the guanine remains unacted on.
H. R. LE S.

Asparagine and Aspartic Acid. By ADOLF JOLLES (*Ber.*, 1901, 34, 386—390. Compare this vol., i, 30).—Aspartic acid, when oxidised with permanganate, gives a quantitative yield of ammonia, but no carbamide. Asparagine gives a 50 per cent. yield of carbamide, and 50 per cent. of ammonia.
T. M. L.

Transformation of *iso*Dialuric Acid into Dialuric Acid. By PAUL KOECH (*Annalen*, 1901, 315, 246—259).—It is well known that *isodialuric* acid and carbamide undergo condensation to uric acid. An attempt to prepare iminouric acid from *isodialuric* acid and guanidine resulted in the production of alloxantin, and this is now found to be due to the fact that, under the influence of bases, *isodialuric* acid becomes transformed into dialuric acid. A description of the varying experimental conditions under which this change takes place constitutes the experimental portion of the paper.
M. O. F.

Condensation of *iso*Dialuric Acid with Thiocarbamide. By CURT VON VOGEL (*Annalen*, 1901, 315, 259—268).—The compound, $C_{16}H_{26}O_{11}N_{12}S_3$, prepared by heating *isodialuric* acid with thiocarbamide and glacial acetic acid on a water-bath, crystallises in spherical aggregates of small, reddish-brown needles; it is practically insoluble in water, dilute acids, alcohol, and ether, but dissolves readily in sodium hydroxide and in concentrated sulphuric acid.

Boiling sodium hydroxide eliminates all the sulphur and a portion of the nitrogen from the substance, producing a sparingly soluble sodium salt, $C_{16}H_{17}O_{18}N_7Na_2$. The compound, $C_4H_5O_5N_3$, obtained by the action of concentrated nitric acid on the condensation product, crystallises in yellow needles; the ammonium, sodium, and silver salts are crystalline.
M. O. F.

Action of Hydrofluosilicic Acid on Potassium Ferrocyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, 25, 158—159).—When solutions of potassium ferrocyanide and of hydrofluosilicic acid are mixed, a greenish coloration is produced, and if air is admitted a blue colour develops. This is a fairly delicate qualitative test. Ex-

periments have shown that either in the cold or at 100° the products formed are Berlin blue and potassium silicofluoride. In the cold, a large excess of the acid is necessary, but at 100° the reaction may be represented by the equation $7\text{H}_4\text{Fe}(\text{CN})_6 + 14\text{H}_2\text{SiF}_6 + \text{O}_2 = \text{Fe}_4(\text{FeC}_6\text{N}_6)_3 + 24\text{HCN} + 14\text{K}_2\text{SiF}_6 + \text{H}_2\text{O}$.
J. J. S.

Mixed Organomagnesium Compounds. By VICTOR GRIGNARD (*Compt. rend.*, 1901, 132, 558—561. Compare *Abstr.*, 1900, i, 382; this vol., i, 250).—The product of the action of an alkyl iodide on magnesium in the presence of anhydrous ether may be either the compound $\text{R}\cdot\text{MgI}$ or a mixture of MgR_2 and magnesium iodide. Although the residue obtained on evaporating the ether has not been isolated in a state of purity, yet indirect evidence exists for believing the product to be $\text{R}\cdot\text{MgI}$. The substances are solid and not spontaneously inflammable in air, and are formed without any deposition of magnesium haloid salt. They react with aldehydes or ketones, giving rise to compounds containing the whole of the halogen present, and these products, when decomposed by water, yield secondary or tertiary alcohols without the evolution of any gaseous hydrocarbon. The compound from magnesium methiodide and acetone crystallises from ether and has the composition $\text{CMe}_3\cdot\text{OMgI}\cdot\text{Et}_2\text{O}$.

The yield of alcohol obtained by this process always exceeds 50 per cent. of the theoretical. Similar results are obtained with the products of the interaction of magnesium and the alkyl bromides. The reaction between magnesium and the haloid ethers of unsaturated radicles takes a different course. When allyl bromide or iodide is employed, the product, being only slightly soluble in ether, is deposited, and, moreover, only half an atomic proportion of the metal is attacked by a mol. proportion of the organic compound. The *organo-magnesium* compound produced crystallises in colourless, flattened needles, and has the composition $\text{C}_3\text{H}_5\text{MgI}\cdot\text{C}_3\text{H}_5\text{I}$. The substance is very unstable, and does not readily react with aldehydes or ketones, the synthesis in this case being less efficient than that due to Saytzeff.
G. T. M.

General Method for the Synthesis of Naphthenes. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1901, 132, 566—568. Compare this vol., i, 210).—The property of hydrogenating benzene to cyclohexane is peculiar to nickel; reduced cobalt and platinum black have a transitory action which is lost after a few minutes; spongy platinum or reduced iron and copper are quite inert. The reaction has been extended to the homologues of benzene and the following naphthenes, *o*- and *m*-dimethylcyclohexanes, and 1:3:5- and 1:2:4-trimethylcyclohexanes, have been prepared from the corresponding benzenoid hydrocarbons. *Ethylcyclohexane*, $\text{C}_6\text{H}_{11}\text{Et}$, boils at 128—129° (corr.), and has a sp. gr. 0.8026; *propylcyclohexane* boils at 153—154° (corr.) and has a sp. gr. 0.8098. A decanaphthene or menthane, $\text{C}_6\text{H}_{10}\text{MePr}^{\text{f}}$, boiling at 166—168° (corr.) is obtained from *p*-cymene. These naphthenes, when heated at 300° in the presence of reduced nickel, undergo decomposition, yielding methane, carbon, and the corresponding benzenoid hydrocarbon.
G. T. M.

Organic Polysulphides and the Polysulphides of Sodium. By J. J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 457—459).—A continuation of earlier work (*Abstr.*, 1900, i, 482). The di-, tri-, and tetra-sulphides of sodium exist as such in alcoholic solution, since they will react then with the nitro-derivatives of aromatic hydrocarbons forming aromatic di-, tri-, and tetra-sulphides. The aromatic tetrasulphides can also be obtained by treating the sodium derivatives of the disulphides with iodine, showing that the constitution of the tetrasulphides is $R \cdot S \cdot S \cdot S \cdot S \cdot R'$ and of sodium tetrasulphide $NaS \cdot S \cdot S \cdot SNa$. If sodium disulphide does not react with these nitro-compounds to form disulphides, it acts as a reducing agent, converting, for example, *m*-dinitrobenzene into *m-m*-dinitroazoxybenzene. R. H. P.

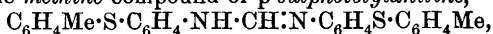
***p*-Toluenesulphinic Acid.** By ERNST VON MEYER with R. NACKE and M. GMEINER (*Chem. Centr.*, 1901, i, 455—456; from *Ber. k. sächs. Ges. Wiss. Math. phys. Cl.*, 52, 124—139; *J. pr. Chem.*, 1901, [ii], 63, 167—183).—*p*-Tolylsulphonocarbinal, $C_6H_4Me \cdot SO_2 \cdot CH_2 \cdot OH$, formed by heating formaldehyde with *p*-toluenesulphonic acid, crystallises from benzene in needles, melts at 90° , is easily soluble in alcohol, chloroform, or ether, and is resolved into its components by boiling water, dry ammonia, or sodium hydroxide solution; on oxidation it forms di-*p*-tolyl-disulphone. The *acetate*, $C_6H_4Me \cdot SO_2 \cdot CH_2 \cdot OAc$, crystallises in prisms and melts at 78° ; the *phosphate* crystallises in long plates and melts at 146° . Di-*p*-tolylsulphonomethylamine, $NH(CH_2 \cdot SO_2 \cdot C_6H_4Me)_2$, formed by dissolving the carbinal in ammonia and precipitating with hydrochloric acid, crystallises in long, slender needles, melts at 158 — 160° and is decomposed by hot sodium hydroxide solution. *p*-Tolylsulphonocarbinyllaniline, $C_6H_4Me \cdot SO_2 \cdot CH_2 \cdot NHPH$, crystallises in slightly yellow, flat needles and melts at 137° . Di-*p*-tolyl-disulphone, $C_{14}H_{14}O_4S_2$, formed by oxidising the carbinal with potassium permanganate dissolved in water or glacial acetic acid, crystallises from acetone in rhombohedra, decomposes at about 210° without melting, is almost insoluble in alcohol, ether, or benzene, and is quickly decomposed by alcoholic solutions of alkalis. By the action of alcoholic ammonia at 130° , ammonium *p*-toluenesulphinate and *p*-toluenesulphonamide are formed, but with phenylhydrazine it yields only phenylhydrazine *p*-toluenesulphinate.

Di-*p*-tolylsulphonohydroxylamine, $OH \cdot N(SO_2 \cdot C_6H_4Me)_2$, prepared by adding solutions of sodium *p*-toluenesulphinate (2 mols.) and sodium nitrite (1 mol.) to cold dilute hydrochloric acid, crystallises from alcohol in needles, melts at 125° , and is decomposed by sodium hydroxide solution. The *benzoyl* derivative, $OBz \cdot N(SO_2 \cdot C_6H_4Me)_2$, obtained by the action of benzoyl chloride on the preceding compound, crystallises from alcohol in rhombohedra and melts at 186° . Tri-*p*-tolylsulphonamide, $N(SO_2 \cdot C_6H_4Me)_3$, formed by the action of nitrous acid on ditolylsulphonohydroxylamine dissolved in alcohol or in glacial acetic acid, or by the action of *p*-toluenesulphonic chloride dissolved in pyridine, or by treating ditolylsulphonohydroxylamine with *p*-toluenesulphinic acid in glacial acetic acid solution, crystallises in rhombic

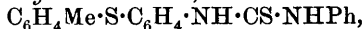
leaflets, melts at 184° and is slightly soluble in alcohol or glacial acetic acid.

p-Tolylsulphonohydroxylamine, $C_6H_4Me \cdot SO_2 \cdot NH \cdot OH$, obtained by adding *p*-toluenesulphonic chloride to an alcoholic solution of hydroxylamine, crystallises from chloroform or benzene in matted needles, melts at 148° , is easily soluble in the ordinary solvents and is readily hydrolysed by aqueous solutions of alkalis. The sodium compound is thrown down as a white precipitate by sodium ethoxide. The dibenzoyl derivative, $C_6H_4Me \cdot SO_2 \cdot NBz \cdot OBz$, crystallises in hexagonal plates and melts at 120° . When *p*-tolylsulphonohydroxylamine is treated with *p*-tolylsulphonic chloride in aqueous solution at 70° , di-*p*-tolyldisulphone is formed.

When aniline *p*-toluenesulphinate is gradually heated to 215° (compare Hälssig, Abstr., 1898, i, 141), it loses water, aniline, sulphur dioxide and traces of toluene, and from the blue mass which is formed, water extracts aniline *p*-toluenesulphonate. The residue when treated with dilute sulphuric acid yields the salt of a base which by the action of ammonia and ether is decomposed, forming *p*-tolyl aminophenyl sulphide, $C_6H_4Me \cdot S \cdot C_6H_4 \cdot NH_2$; this crystallises from ether in flat needles, melts at 72° , is a feeble base and forms salts which are soluble in water. The sulphate crystallises in leaflets, the hydrochloride in long needles. The methine compound of *p*-sulphotolylaniline,



prepared by means of ethyl orthoformate, crystallises in needles. *p*-Thiotolylanilinephenylthiocarbimide,



obtained by means of phenylthiocarbimide, crystallises in colourless needles and melts at 161° .

Tetramethylammonium *p*-toluenesulphinate decomposes above 180° , forming trimethylamine and methyl-*p*-tolylsulphone, $C_7H_7SO_2Me$, melting at 86° . The tetraethyl salt decomposes in a similar way, forming ethyl-*p*-tolylsulphone which melts at 57° . E. W. W.

Formation of a Hydrocarbon, $C_{12}H_{16}$, from Quinitol. By RICHARD WILLSTÄTTER and RUDOLF LESSING (*Ber.*, 1901, 34, 506—508).—When either the *cis*- or *trans*- form of quinitol (Baeyer, Abstr., 1894, i, 174) is heated with 60 per cent. sulphuric acid at 100° , a hydrocarbon, $C_{12}H_{16}$, is obtained which boils at 230 — 233° under 710 mm. pressure. It is stable to permanganate, but is attacked readily by bromine, hydrogen bromide being evolved; it can be nitrated with a mixture of nitric and sulphuric acids, and the nitro-derivative formed is reduced by tin and hydrochloric acid to an amine, which forms a crystalline hydrochloride, and can be diazotised and converted into azo-dyes. Probably, therefore, the hydrocarbon contains a benzene ring, and is phenylcyclohexane, $CH_2 \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} CHPh$.

C. F. B.

isoStilbene. By JOHANNES WISLICENUS [and MORITZ JAHRMARKT] (*Chem. Centr.*, 1901, i, 463—464, from *Ber. k. sächs. Ges. Wiss. Math. phys. Cl.*, 1900, 52, 117—123. Compare Abstr., 1896, i, 98; 1897, i, 533).—Bromoisostilbene, $\begin{smallmatrix} HCPH \\ | \\ PhCBr \end{smallmatrix}$, prepared by the action of potassium

hydroxide on α -stilbene dibromide, crystallises in long, colourless needles, melts at 19° , and is not readily attacked by alcoholic potash.

*iso*Stilbene, $\begin{array}{c} \text{PhCH} \\ | \\ \text{HCPh} \end{array}$, obtained, together with stilbene, by reducing bromo*iso*stilbene with zinc dust and glacial acetic acid or alcohol, or with sodium amalgam and glacial acetic acid, is an oil which on distillation under atmospheric pressure is converted into ordinary stilbene, the boiling point rising from 270° to 300° , but it boils at $139\text{--}145^\circ$ under 12 mm. pressure without change. It readily changes into stilbene on exposure to sunlight, or by the action of traces of bromine or iodine, and yields 83 per cent. of *iso*stilbene dibromide, $\begin{array}{c} \text{CPhHBr} \\ | \\ \text{CPhBrH} \end{array}$, when it is dissolved in carbon disulphide and the solution added to cooled bromine in the dark. E. W. W.

The Two Stereoisomeric Diphenyldinitroethylenes (Dinitrostilbenes, Tolane Dinitrites). By JULIUS SCHMIDT (*Ber.*, 1901, 34, 619—623).—When the gas evolved on warming arsenious oxide with concentrated nitric acid is passed into a cold ethereal solution of tolane, a mixture of nearly equal quantities of two *diphenyldinitroethylenes* (α and β) is obtained. The α -compound, being the less soluble, separates first, and crystallises from alcohol in bright yellow, lustrous needles, is not volatile with steam, and melts at $186\text{--}187^\circ$; the β -form crystallises from alcohol in lustrous, yellow pyramids and melts at $105\text{--}107^\circ$. Both compounds, in spite of their ethylenoid linking, fail to combine with bromine at 100° . Since the β -compound decomposes at 150° , whereas the α -compound is much more stable, the former probably has the configuration $\begin{array}{c} \text{Ph}\cdot\text{C}\cdot\text{NO}_2 \\ | \\ \text{NO}_2\cdot\text{C}\cdot\text{Ph} \end{array}$, and the latter, $\begin{array}{c} \text{Ph}\cdot\text{C}\cdot\text{NO}_2 \\ | \\ \text{Ph}\cdot\text{C}\cdot\text{NO}_2 \end{array}$. On reduction with zinc dust and acetic acid, both forms yield 2:3:5:6-tetraphenylpiperazine (this vol., i, 295). W. A. D.

Action of Nitrous Acid on Stilbene; *s*-Diphenyldinitroethane (Stilbene Dinitrite). By JULIUS SCHMIDT (*Ber.*, 1901, 34, 623—626).—On passing the nitrous fumes evolved on warming arsenious oxide with nitric acid into a well cooled ethereal solution of stilbene, the *nitrosite*, $\begin{array}{c} \text{CHPh} \\ | \\ \text{CHPh} \end{array} > \text{N}_2\text{O}_3$, separates in white crystals which soften at 160° and melt and decompose at $195\text{--}197^\circ$; the compound melting at 132° described by Angeli (*Abstr.*, 1894, i, 75) could not be obtained. On dissolving the nitrosite in boiling glacial acetic acid, it is converted into *s*-*diphenyldinitroethane*, which crystallises in white, silky needles and melts and decomposes at $235\text{--}236^\circ$. Benzaldehyde was also formed (isolated as the phenylhydrazone) and a small quantity of a crystalline substance melting at $145\text{--}146^\circ$. W. A. D.

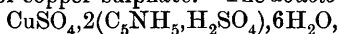
Compounds of Cupric Salts with Organic Bases. By DANIEL TOMBECK (*Ann. Chim. Phys.*, 1901, 22, [vii], 113—144. Compare *Abstr.*, 1898, i, 566; this vol., i, 135).—The compound, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2, 2\text{NH}_2\text{Ph}, \text{H}_2\text{O}$,

produced by adding aniline to an aqueous solution of copper acetate placed in an inert atmosphere, separates from solution in small, dark green needles, which rapidly turn brown on exposure to air; it dissolves in water or alcohol, the aqueous solution rapidly decomposing, especially on raising the temperature.

The *double salt*, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NH}_3\text{Ph} \cdot \text{C}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$, formed by acidifying the solution of the preceding compound with acetic acid, crystallises in light green, silky needles soluble in water or alcohol without decomposition and melting in its own water of crystallisation.

The *compound*, $\text{Cu}(\text{HCO}_2)_2 \cdot 2\text{NH}_2\text{Ph}$, resembles the corresponding acetate, and is formed by adding powdered copper formate to aniline, the corresponding *oxalate*, $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_2\text{Ph}$, being obtained in a similar manner.

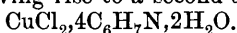
The *compound*, $\text{CuSO}_4 \cdot 4\text{C}_5\text{NH}_5$, is a dark blue, amorphous powder, produced when anhydrous copper sulphate is placed in a dry atmosphere containing pyridine vapour; the hydrated form of this substance crystallises with $4\text{H}_2\text{O}$, and is obtained by adding pyridine to a saturated solution of copper sulphate. The *double salt*,



is formed by adding sulphuric acid to the aqueous solution of the preceding compound until its colour changes from blue to green; it separates in blue, prismatic crystals soluble in water or dilute sulphuric acid, the solution in the latter case being almost colourless. The *nitrate*, $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{C}_5\text{NH}_5 \cdot 6\text{H}_2\text{O}$, crystallises in large, indigo-blue prisms, and loses pyridine at the ordinary temperature, passing into the *compound* $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{C}_5\text{NH}_5 \cdot 4\text{H}_2\text{O}$.

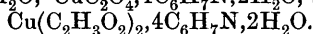
With the acetate, formate, and oxalate of copper, pyridine forms the following *compounds* respectively: $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{C}_5\text{NH}_5$; $\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{C}_5\text{NH}_5 \cdot 4\text{H}_2\text{O}$, and $\text{CuC}_2\text{O}_4 \cdot 4\text{C}_5\text{NH}_5 \cdot 2\text{H}_2\text{O}$; the *double acetate*, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2(\text{C}_5\text{NH}_5 \cdot \text{C}_2\text{H}_4\text{O}_2) \cdot 2\text{H}_2\text{O}$, being produced by the action of acetic acid on a solution of the first of these substances.

The *compound*, $\text{CuCl}_2 \cdot 2\text{C}_6\text{H}_7\text{N} \cdot 2\text{H}_2\text{O}$, obtained in light blue needles when an alcoholic solution of cupric chloride is treated with picoline, dissolves in this base, giving rise to a second *derivative*,



The *double salt*, $\text{CuCl}_2 \cdot 2(\text{C}_6\text{H}_7\text{N} \cdot \text{HCl}) \cdot 2\text{H}_2\text{O}$, produced by adding dilute hydrochloric acid to solutions of the preceding compounds, forms reddish-yellow crystals soluble in water or alcohol. Anhydrous copper sulphate absorbs the vapour of picoline, yielding the compound $\text{CuSO}_4 \cdot 4\text{C}_6\text{H}_7\text{N}$, the *hydrated derivative*, $\text{CuSO}_4 \cdot 2\text{C}_6\text{H}_7\text{N} \cdot 5\text{H}_2\text{O}$, being produced by the addition of the base to a saturated solution of the copper salt.

The following *compounds* are obtained respectively from picoline and copper nitrate, oxalate, or acetate: $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{C}_6\text{H}_7\text{N} \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{C}_6\text{H}_7\text{N} \cdot 4\text{H}_2\text{O}$, $\text{CuC}_2\text{O}_4 \cdot 4\text{C}_6\text{H}_7\text{N} \cdot 2\text{H}_2\text{O}$, and

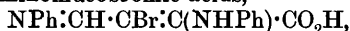


The *compounds* of the copper salts with α -lutidine resemble those of its lower homologue, and are produced by similar methods; the following have been prepared: $\text{CuCl}_2 \cdot 2\text{C}_7\text{H}_9\text{N} \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 4\text{C}_7\text{H}_9\text{N} \cdot 2\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 4\text{C}_7\text{H}_9\text{N}$, $\text{CuSO}_4 \cdot 2\text{C}_7\text{H}_9\text{N} \cdot 5\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{C}_7\text{H}_9\text{N} \cdot 6\text{H}_2\text{O}$, $\text{CuC}_2\text{O}_4 \cdot 2\text{C}_7\text{H}_9\text{N} \cdot 2\text{H}_2\text{O}$.
G. T. M.

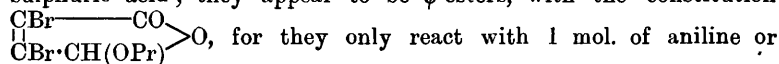
A New Method of Preparing *p*-Alkyloxybenzylanilines and their Homologues. By PAUL FRITSCH (*Annalen*, 1901, 315, 138—143).—When anhydroformaldehydeaniline is added slowly to a mixture of a phenol ether and sulphuric acid, the corresponding *p*-alkyloxybenzylaniline is produced, the best yield being obtained with 83·5 per cent. acid. By this method the author has prepared *p*-methoxybenzylaniline, *p*-ethoxybenzylaniline, *p*-methoxybenzyl-*o*-toluidine and *p*-ethoxybenzyl-*o*-toluidine; they melt at 64·5°, 65°, 55°, and 53° respectively.

M. O. F.

Action of Primary Amines on Mucobromic and Mucochloric Acids and their Esters. By HUGO SIMONIS (*Ber.*, 1901, 34, 509—519).—Mucobromic and mucochloric acids, $\text{CHO}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CO}_2\text{H}$, &c. (Abstr., 1899, i, 741), react vigorously with aniline or *p*-toluidine in the presence of a little absolute alcohol, mucochloric acid especially so; a freezing mixture must be employed to moderate the violence of the action. With 1 mol. of the base, NH_2Ph , &c., substituted iminomucobromic acids, $\text{NPh}\cdot\text{CH}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CO}_2\text{H}$, &c., are formed; with 2 mols. substituted aminoiminomucobromic acids,



which are yellow, and lose carbon dioxide when heated, forming substituted α -bromo- β -aminoiminoacraldehyde, $\text{NPh}\cdot\text{CH}\cdot\text{CBr}\cdot\text{CH}\cdot\text{NPh}$; with an excess of the base, preferably 5—6 mols., the aniline salt of the last acid, $\text{NPh}\cdot\text{CH}\cdot\text{CBr}\cdot\text{C}(\text{NPh})\cdot\text{CO}_2\cdot\text{NH}_2\text{Ph}$, which is yellow, and is decomposed into the acid and aniline by water. Various esters of mucobromic and mucochloric acids were prepared by boiling the acids for 2 hours with excess of the alcohol and a few drops of strong sulphuric acid; they appear to be ψ -esters, with the constitution



p-toluidine, forming phenylaminomucobromates, $\begin{array}{c} \text{C}(\text{NPh})\text{---CO} \\ || \quad \quad \quad \diagup \text{O} \\ \text{CBr}\cdot\text{CH}(\text{OPr}) \end{array}$, &c.

The compounds prepared are enumerated below, with the temperatures at which they decompose (or melt, when that is stated expressly).

Phenyliminomucobromic acid, 126°; *phenyliminophenylaminomucobromic acid*, 135—140°, its silver salt and yellow monobenzoyl derivative melting at 103—105°, and *aniline salt*; also α -bromo- β *phenylaminophenyliminoacraldehyde*, 144—146°; *phenyliminomucochloric acid*, 132°; *phenyliminophenylaminomucochloric acid*, 150°; *p*-tolylimino-*p*-tolylaminomucobromic acid, 165—168°.

Propyl and allyl mucobromates, melting at 31·5° and 41° respectively; *methyl, ethyl, propyl, and allyl mucochlorates*, all liquid; *methyl, ethyl, and propyl phenylaminomucobromates*, melting at 117°, 114°, and 80° respectively; *methyl mucochlorate*, crystalline; *methyl-p*-tolylaminomucochlorate, melting at 118°; *ethyl-m-xylaminomucochlorate*, melting at 114°.

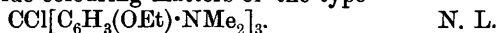
C. F. B.

New Colouring Matters. By EDOUARD GRIMAUX and LÉON LEFÈVRE (*Bull. Soc. Chim.*, 1901, [iii], 25, 213—214).—Various azo-colouring matters, details of which are not given in the paper, are obtained by the action of phenols, naphthols, amines, &c., on the products of diazo-

tisation of derivatives of triphenylmethane and its homologues. Monoamines, diamines, and triamines have been experimented with.

Colouring matters of the resaurine and resoxeine classes are obtained (1) by the action of sulphuric acid on resorcinol at 100° ; (2) by the action of nitric and sulphuric acids on resorcinol; (3) by brominating the latter derivative; (4) by the action of aniline on resoxeine at 150° ; (5) by the alkylation of resoxeine and of Nencki's resaurine; (6) by brominating the preceding; (7) by brominating resaurine; (8) by the action of aniline on resaurine at 150° . N. L.

Blue Colouring Matters derived from Triphenylmethane. By EDOUARD GRIMAU (Bull. Soc. Chim., 1901, [iii], 25, 215).—The action of carbonyl chloride on *m*-dimethylaminomethoxybenzene and its homologues in the presence of aluminium chloride results in the formation of soluble, blue colouring matters of the type



Red Colouring Matters derived from Triphenylmethane. By EDOUARD GRIMAU (Bull. Soc. Chim., 1901, [iii], 25, 215—216).—Fluorescent, red colouring matters are obtained by heating *m*-dimethylaminomethoxybenzene or its homologues with phthalic anhydride at 175 — 180° . N. L.

Derivatives of Triphenylmethane. By EDOUARD GRIMAU (Bull. Soc. Chim., 1901, [iii], 25, 216—217).—A blue colouring matter is formed by the oxidation of *o*-dimethylaminomethoxybenzene or its next higher homologue. The red colouring matter obtained by the action of phthalic anhydride on *m*-dimethylaminomethoxybenzene or its homologues (preceding abstract) is converted by the action of sulphuric acid into a new colouring matter of a less violet tint. Substituted rhodamines behave in a similar manner. When treated with carbon tetrachloride, *o*-dimethylaminomethoxybenzene yields a colourless compound which furnishes a violet colouring matter on oxidation with lead peroxide. *m*-Dimethylaminoethoxybenzene forms a garnet-coloured dye when treated with arsenic acid at 180 — 185° . N. L.

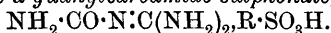
Preparation of *m*-Alkylaminophenols. By EDOUARD GRIMAU (Bull. Soc. Chim., 1901, [iii], 25, 217—218).—*m*-Dimethylaminophenol and *m*-diethylaminophenol are obtained by heating dimethylamine and diethylamine respectively with resorcinol at 200° . When heated with dimethylamine or diethylamine at 200 — 255° , fluorescein yields colouring matters resembling the rhodamines. A green colouring matter resembling malachite-green is obtained by oxidising the product of the condensation of dimethylaminomethoxybenzene or its homologues with benzaldehyde or nitrobenzaldehyde. N. L.

Colouring Matters derived from *m*-Dialkylaminoalkoxybenzenes. By EDOUARD GRIMAU (Bull. Soc. Chim., 1901, [iii], 25, 219—220).—The hydrochloride of 4-nitroso-1-dimethylamino-3-ethoxybenzene yields (1) an ethoxyindophenol when reduced with zinc dust and subsequently oxidised with potassium dichromate in presence of α -naphthol; (2) an ethoxytolylene-blue when heated with *m*-tolylene-diamine; (3) a blue colouring matter, an ethoxy-derivative of

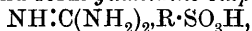
Meldola's blue, by heating with β -naphthol in acetic acid solution; (4) safranines, when heated with zinc dust and subsequently oxidised in presence of primary amines; (5) an ethoxylated gallocyanin when boiled with tannin; (6) a blue colouring matter when heated with resorcinol; (7) a blue colouring matter when reduced with zinc dust and treated with *m*-dimethylaminophenol in alkaline solution.

N. L.

Action of Aromatic Sulphonic Chlorides on Carbamide. By IRA REMSEN and W. W. GARNER (*Amer. Chem. J.*, 1901, 25, 173—190).—The condensation product obtained by heating carbamide, $2\text{CO}(\text{NH}_2)_2$, with a sulphonic chloride, $\text{R}\cdot\text{SO}_2\text{Cl}$ (compare Elander, *Abstr.*, 1881, 164), is shown to be a *guanylcarbamide sulphonate*,



These can be synthesised from guanylcarbamide and the sulphonic acids, and yield, as a precipitate, the pink copper derivative of guanylcarbamide when heated with sodium hydroxide and copper sulphate. From this copper derivative, guanylcarbamide itself can be obtained, and indeed this new method of preparing it is the best available at present. These guanylcarbamide sulphonates evolve carbon dioxide and ammonia, and form *guanidine sulphonates*,



(identical with products synthesised from guanidine carbonate and the sulphonic acids), when they are heated with dilute hydrochloric acid at 170 — 180° ; with fuming nitric acid, they yield nitroguanidine; when boiled with aqueous potassium carbonate, they yield ammonia, carbon dioxide, and guanidine sulphonates, and when boiled with aqueous barium hydroxide they yield ammonia, barium carbonate, and barium sulphonates.

In the case of *p*-toluenesulphonic chloride, its action on carbamide was also tried in alcoholic solution; the product was carbamide *p*-toluenesulphonate.

The following substances were prepared; the numbers are melting points: *Guanylcarbamide benzenesulphonate*, 216° ; *p*-toluenesulphonate, 224° ; *o*-toluenesulphonate, 205° ; α -naphthalenesulphonate, 223° ; β -naphthalenesulphonate, 237° . *Guanidine benzenesulphonate*, 206° ; *p*-toluenesulphonate, 206° ; α -naphthalenesulphonate; β -naphthalenesulphonate, 259° .

C. F. B.

Action of Aromatic Sulphonic Chlorides on Thiocarbamide. By IRA REMSEN and H. J. TURNER (*Amer. Chem. J.*, 1901, 25, 190—202).—When a sulphonic chloride, $\text{R}\cdot\text{SO}_2\text{Cl}$, is warmed with thiocarbamide, $\text{CS}(\text{NH}_2)_2$, in alcoholic solution, needles of dithiocarbamide dichloride, $\text{CCl}(\text{NH}_2)_2\cdot\text{S}\cdot\text{S}\cdot\text{CCl}(\text{NH}_2)_2$, separate (the yield can be increased by diluting with ether), whilst a disulphoxide, $\text{SRO}\cdot\text{SRO}$ (or thiosulphonate, $\text{R}\cdot\text{SO}_2\cdot\text{SR}$) remains in solution and can be precipitated by diluting with water; sulphur is also formed. Apparently these disulphoxides are best prepared in this way. The reaction was carried out in the case of the benzene and *p*-toluene derivatives.

With ammonium thiocyanate, benzenesulphonic chloride yields no well characterised product.

From potassium benzene- or *p*-toluene-sulphinat and dithiocarbamide

dichloride in alcoholic solution, the disulphoxide is obtained, along with another crystalline product, free from nitrogen. The product melted at 99.5° and 155 — 158° in the two cases respectively. A hydrosulphide and sulphur are also formed. C. F. B.

Action of the Chlorides of *o*-Sulphobenzoic and of *p*-Nitro-*o*-sulphobenzoic Acids on Carbamide. By WILLIS B. HOLMES (*Amer. Chem. J.*, 1901, 25, 202—216).—Symmetrical (stable) *o*-sulphobenzoic chloride, $\text{COCl}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$, is obtained best by dissolving the mixture of isomeric chlorides (Remsen, Abstr., 1895, i, 472; List and Stein, Abstr., 1898, i, 584) in ether and shaking with ammonia, which is added gradually until its odour is just perceptible after shaking. The unsymmetrical (labile) chloride, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CCl}_2 \\ \text{SO}_2 \end{smallmatrix}\rangle\text{O}$, is obtained best by heating potassium *o*-sulphobenzoate with phosphorus oxychloride at 135° ; it melts at 40° , not at 21° . A mixture of the two chlorides crystallises like a homogeneous substance, and has melting point 21° .

When either of these two chlorides is heated at 100° with carbamide (1 : 4 mols.) for several days, a product is obtained that could not be isolated but yielded ammonium benzoylcarbamide-*o*-sulphonate, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{NH}_4$, when dissolved in water. This salt is converted by cold aqueous barium hydroxide into the barium salt; boiling dilute aqueous potassium hydroxide eliminates ammonia and carbon dioxide, and forms the potassium salt of *o*-benzaminosulphonic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{K}$; boiling dilute hydrochloric acid hydrolyses it to *o*-sulphobenzoic acid. The same product is obtained from both chlorides, and in the same yield, namely 55 per cent. of the theoretical. From the isomeric *p*-nitro-*o*-sulphobenzoic chlorides, analogous derivatives were obtained. The substances prepared are enumerated below, with their melting points and water of crystallisation.

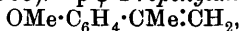
Benzoylcarbamide-o-sulphonic acid, crystalline, very soluble in water; *ammonium*, 266° , *barium* $\text{BaA}_2\cdot 2\text{H}_2\text{O}$, *potassium*, 286° , *sodium*, $\text{NaA}\cdot\text{H}_2\text{O}$, *lead*, $\text{PbA}_2\cdot 3\text{H}_2\text{O}$, *copper*, $\text{CuA}_2\cdot 6\text{H}_2\text{O}$, and *silver* salts. *p-Nitrobenzoylcarbamide-o-sulphonic acid*, very soluble; its *ammonium*, 273° , *barium*, $\text{BaA}_2\cdot 2\text{H}_2\text{O}$, *potassium*, $\text{KA}\cdot\text{H}_2\text{O}$, *sodium*, $\text{NaA}\cdot\text{H}_2\text{O}$ or $4\text{H}_2\text{O}$, *lead*, $\text{PbA}_2\cdot 5\text{H}_2\text{O}$, *copper*, $\text{CuA}_2\cdot 3\text{H}_2\text{O}$, and *silver* salts [$\text{A} = \text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\cdot$ and $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{SO}_3\cdot$ respectively]. C. F. B.

Chloro-derivatives of *o*-Benzoicsulphinide. By C. MASELLI (*Gazzetta*, 1900, 30, ii, 529—539).—*Chlorobenzalsultim* ("chloro- ψ -saccharin"), $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CCl} \\ \text{SO}_2 \end{smallmatrix}\rangle\text{N}$, prepared by passing chlorine into an aqueous solution of *o*-benzoicsulphinide, is slightly soluble in chloroform, carbon tetrachloride, benzene, or *p*-xylene, more so in light petroleum or toluene, and separates from the last-named solvent in white crystals melting at about 170° . When heated at 190° in an atmosphere of carbon dioxide, it sublimes in long acicular crystals with partial decomposition. It has the normal molecular weight in freezing acetic acid, and by the action of alcohol is converted into ethoxybenzalsultim ("ethoxy- ψ -saccharin"). T. H. P.

Preparation of Anils [Phenylimides] of Acid Cyanides. By FRANZ SACHS [and in part EDUARD BRY and C. MEREDITH WHITTAKER] (*Ber.*, 1901, 34, 494—503).—Substituted aromatic aminobenzyl cyanides, $\text{CN}\cdot\text{CHPh}\cdot\text{NHR}$, can be obtained by heating benzaldehyde cyanohydrin, $\text{CN}\cdot\text{CHPh}\cdot\text{OH}$, with an aromatic amine, NH_2R , and a little alcohol at 100° (Tiemann and Piest, *Abstr.*, 1883, 198). They can be oxidised in boiling acetone solution by potassium permanganate to yellow substituted iminobenzoyl cyanides, $\text{CN}\cdot\text{CPh}\cdot\text{NR}$; when $\text{R}=\text{C}_6\text{H}_4\cdot\text{NMe}_2$, the oxidation can even be effected by aspirating air through the boiling solution of the base. (This action of permanganate on the saturated grouping $>\text{CH}\cdot\text{NH}\cdot$, which it converts readily into the unsaturated one, $>\text{C}\cdot\text{N}\cdot$, is in strong contrast to its action on the typical unsaturated hydrocarbon grouping; in the latter case, an unsaturated grouping, $>\text{C}:\text{C}<$, is converted into a saturated one, $>\text{C}(\text{OH})\cdot\text{C}(\text{OH})<$, &c.) The same iminobenzoyl cyanides are obtained by heating benzyl cyanide with an aromatic nitroso-derivative to boiling in alcoholic solution, and adding a little sodium carbonate solution; so obtained, however, they sometimes differ slightly from those obtained by the first method, and possibly are stereoisomeric with them. They can be reduced by zinc and ammonium or calcium chloride in alcoholic or acetone solution, but it is difficult satisfactorily to isolate the products.

Phenyliminobenzoyl cyanide, $\text{R}=\text{Ph}$, when made by the first method, melts at 72° and is not hydrolysed by sulphuric acid; when made by the second method it contains $\frac{3}{4}\text{H}_2\text{O}$ in addition, melts at 135° , and is converted into *phenyliminobenzoylformamide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CPh}\cdot\text{NPh}$, melting at 141° , when it is dissolved in strong, cold sulphuric acid and the solution poured into water. *p-Tolyliminobenzoyl cyanide*, $\text{R}=\text{CH}_2\text{Ph}$, melts at 96° when made by the first method; when made by the second method, it contains $\frac{1}{4}\text{H}_2\text{O}$ in addition, and melts at $93\text{--}94^\circ$. *o-Tolyliminobenzoyl cyanide* has the same composition when made by either method, and melts at 85° ; *o-tolylaminobenzoyl cyanide* melts at 71° . *p-Dimethylaminophenyliminobenzoyl cyanide*, $\text{R}=\text{C}_6\text{H}_4\cdot\text{NMe}_2$ (4-dimethylamidophenyl- μ -cyanazomethinephenyl, *Abstr.*, 1899, i, 884) was obtained by the first method from *p-dimethylaminophenylaminobenzoyl cyanide*, which is red, and melts at 104° . *Phenylimino-p-nitrobenzoyl cyanide*, $\text{CN}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{NPh}$, was obtained by the second method from *p-nitrobenzoyl cyanide*; it is yellow, and melts at 130° ; the homologous *p*- and *o-tolyl* compounds are orange coloured, and both melt at $121\text{--}122^\circ$.
C. F. B.

An Isomeride of Anethole and the Constitution of the latter Compound. By AUGUSTE BÉHAL and TIFFENEAU (*Compt. rend.*, 1901, 132, 561—563).—*p-ψ-Propenylanisole*,



and a bimolecular substance are produced simultaneously by the condensation of ethyl anisate with magnesium methiodide, the two substances being separated by distilling the product in steam, when the former distils over, whilst the polymeride remains in the residue.

p-ψ-Propenylanisole melts at 32° and boils at 222° under the ordinary pressure; it dissolves in alcohol, but is almost insoluble in water, and

has an odour intermediate between those of anethole and estragole. The polymeride crystallises from absolute alcohol in aggregates of needles melting at 58° , and distils without alteration in a vacuum; when heated under the ordinary pressure, the temperature rises to 350° and then falls, a volatile product being obtained which, when rectified, distils at $215\text{--}230^{\circ}$ and yields, on cooling, crystals of the unimolecular substance melting at 32° and boiling at 222° . The bimolecular substance does not combine additively with bromine, a fact which indicates that the ethylene linking is involved in the polymeric change.

Anethole and its polymeride are produced by the action of magnesium ethiodide, this synthesis indicating that the unimolecular compound contains a propenylic chain, and possesses the constitution represented by the formula $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHMe}$. Bougault (Abstr., 1900, i, 495) showed that the aldehyde formed from anethole by the action of iodine and mercuric oxide in the presence of alcohol has the constitution $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{CHO}$. It follows that this condensation has been accompanied by a change of the propenylic chain into an *iso*-propyl grouping. A similar transformation is observed on treating *p*- ψ -propenylanisole in a like manner, the product being a *ketone*, to which the constitution $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{COMe}$ is given for the following reasons. The new compound boils at 264° , whilst Bougault's isomeric aldehyde boils at 255° ; it yields an unstable sodium hydrogen sulphite compound, and an oxime crystallising in fasciculated needles melting at 72° . The ketonic nature of the substance is further demonstrated by the fact that it does not yield an acid on treatment with oxidising agents or alcoholic potassium hydroxide. It does not develop a coloration with a sulphurous acid solution of magenta, and is decomposed by alkali hypobromites into bromoform and anisic acid. G. T. M.

Aromatic Tellurium Compounds. By E. ROHRBAECH (*Annalen*, 1901, 315, 9—18. Compare Rust, Abstr., 1898, i, 137).—*p*-**Telluroanisole**, $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, obtained from dichlorotelluroanisole (*loc. cit.*) by the action of zinc dust on a boiling solution in benzene, separates from dilute alcohol in lustrous, reddish-brown crystals and melts at 50° ; chlorine regenerates dichlorotelluroanisole, and bromine gives rise to the dibromide. Telluroanisole dissolves in hot dilute nitric acid, becoming converted into the dinitrate, which melts at 126° (*loc. cit.*).

p-**Tellurophenetole**, $\text{Te}(\text{C}_6\text{H}_4\cdot\text{OEt})_2$, prepared from dichlorotellurophenetole, crystallises in yellow plates and melts at 64° . The position occupied by the tellurium is indicated by the fact that when dichlorotellurophenetole is heated in a sealed tube at 200° it is resolved into tellurium and *p*-chlorophenetole.

Attempts to prepare a thio-compound corresponding to tellurophenetole by the action of tellurium tetrachloride on thiophenetole were unsuccessful; either no change occurred, or the action was so vigorous that tellurium was precipitated. Tellurium tetrachloride and thiophenol give phenyl disulphide, tellurium, and hydrogen chloride.

Ditelluroanisyl trisulphide, $\text{S}(\text{TeS}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$, prepared by the action

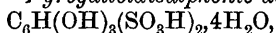
of colourless ammonium hydrogen sulphide on dichlorotelluroanisole in alcohol, crystallises from alcohol in small, dark red needles and melts at 61° . *Ditellurophenetyl trisulphide*, $S(\text{TeS}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, crystallises from alcohol in small, reddish-brown needles and melts at 114° . *Ditellurophenetyl pentasulphide*, $S(\text{TeS}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, obtained from dichlorotellurophenetole and yellow ammonium sulphide, crystallises from alcohol in silky, reddish-brown needles and melts at 92° .

Dichlorotelluromethyl p-phenetyl ketone, $\text{TeCl}_2(\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, produced by the action of tellurium tetrachloride on *p*-phenetyl methyl ketone in ether, crystallises from a mixture of ether and chloroform in small, white needles, which become black at 184° and melt, evolving gas, at 212 — 213° .

Dichlorotelluromethyl m-xyllyl ketone, $\text{TeCl}_2(\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3\text{Me}_2)_2$, crystallises in small, lustrous needles and melts at 180° . *Dichlorotelluromethyl ψ -cumyl ketone*, $\text{TeCl}_2(\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3)_2$, also forms white needles and melts at 188° . *Dichlorotelluroacetocumene*, $\text{TeCl}_2(\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{Pr}^{\beta})_2$, melts at 183° .

Dichlorotelluromethyl α -naphthyl ketone, $\text{TeCl}_2(\text{CH}_2\cdot\text{CO}\cdot\text{C}_{10}\text{H}_{17})_2$, prepared from tellurium tetrachloride and α -naphthyl methyl ketone, crystallises from chloroform and melts at 203 — 204° . M. O. F.

Pyrogallolsulphonic Acids. By MARCEL DELAGE (*Compt. rend.*, 1901, 132, 421—423).—*Pyrogalloldisulphonic acid*,



is obtained in the form of felted, hygroscopic needles by treating pyrogallol with ordinary concentrated sulphuric acid as in the preparation of the monosulphonic acid (compare Abstr., 1900, i, 595), adding to the product fuming sulphuric acid, subsequently diluting the mixture with water, and allowing the solution to crystallise in a dry atmosphere. When the crystals are kept in a desiccator over sulphuric acid they effloresce, losing $2\text{H}_2\text{O}$.

Barium pyrogalloldisulphonate, $\text{C}_6\text{H}(\text{OH})_3(\text{SO}_3)_2\text{Ba}\cdot\frac{1}{2}\text{H}_2\text{O}$, separates in well-defined, light yellow crystals; the *calcium* salt is obtained as a pale, yellowish-white, crystalline powder containing $4\text{H}_2\text{O}$, and losing this by efflorescence on exposure to air; it is less stable than the barium compound, being partially decomposed by repeated crystallisation.

G. T. M.

3:4:3':4'-Tetramethoxystilbene. By W. FEUERSTEIN (*Ber.*, 1901, 34, 415—416).—Veratrole readily condenses with chloral hydrate in a similar manner to other phenol ethers (Elbs, Abstr., 1893, i, 271) to form *tetramethoxydiphenyltrichloroethane*, which is readily reduced by zinc dust to *tetramethoxystilbene*, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_3(\text{OMe})_2$; this crystallises in plates possessing a strong violet fluorescence and melting at 155 — 156° .

A. H.

Phenylmethylallylcarbinol. By ALEXANDER ARBUSOF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 38—45).—*Phenylmethylallylcarbinol*, $\text{C}_3\text{H}_5\cdot\text{CMePh}\cdot\text{OH}$, obtained by the action of zinc or magnesium on acetophenone and allyl iodide in ethereal solution, is a mobile, highly

refractive liquid, insoluble in water, and boiling at $217-223^{\circ}$ (uncorr.); it has the sp. gr. 0.99934 at $20^{\circ}/0^{\circ}$ and 1.00040 at $20^{\circ}/20^{\circ}$. When gently oxidised with potassium permanganate solution, it yields the *trihydric alcohol* of the constitution $\text{OH} \cdot \text{CMePh} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, in the form of a syrupy liquid readily soluble in water, alcohol, or ether, whilst more energetic oxidation gives β -phenylmethylhydracrylic acid, $\text{C}_{10}\text{H}_{12}\text{O}_3$, forming stellate aggregates of acicular crystals melting at $50-53^{\circ}$; the *calcium*, with $2\frac{1}{2}\text{H}_2\text{O}$, *silver* and *zinc*, with $2\text{H}_2\text{O}$, salts of the acid were analysed. T. H. P.

Derivatives of Helicin. By EMIL FISCHER (*Ber.*, 1901, 34, 629—631).—*Helicin cyanhydrin*, $\text{CN} \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_{11}\text{O}_5$, prepared by the action of hydrogen cyanide on an aqueous solution of helicin, crystallises from hot water in square tablets, melts and decomposes at 176° , and dissolves readily in warm alcohol or water, but on boiling the solution is rapidly decomposed into helicin and hydrogen cyanide, and could not therefore be hydrolysed to the acid or to dextrose and salicylaldehyde cyanohydrin.

a-Phenyl-*o*-glucocoumaronitrile, $\text{CN} \cdot \text{CPh} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_{11}\text{O}_5$, prepared by condensing helicin with benzyl cyanide, crystallises from dilute alcohol in minute, felted needles and melts at $175-176^{\circ}$.

T. M. L.

Nitration of *o*-Chloro- and *o*-Bromo-benzoic Acids. By ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 462—463).—*2*-Chloro-3-nitrobenzoic acid, which melts at 185° , has been separated by the fractional crystallisation of the potassium salts from the 2:5-acid, which is the principal product of the nitration of *o*-chlorobenzoic acid (*Abstr.*, 1900, i, 388). *2*-Bromo-3-nitrobenzoic acid melts at 191° , and is obtained in a similar manner to the analogous chloro-acid.

R. H. P.

Condensation of Benzaldehydecyanohydrin with Urethane. By FRITZ LEHMANN (*Ber.*, 1901, 34, 366—377).—By heating together mol. proportions of benzaldehyde and urethane, Bischoff's benzyldenediurethane (*Abstr.*, 1874, 890) is produced, but in presence of zinc chloride the product is *urethanophenylacetoneitrile*, $\text{CN} \cdot \text{CHPh} \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, which crystallises from light petroleum, melts at 83° , is not acted on by acetic anhydride, and does not dissolve in dilute acids or alkalis, but is converted into the amide by concentrated sulphuric or hydrochloric acid. *Urethanophenylacetamide*, $\text{NH}_2 \cdot \text{CO} \cdot \text{CHPh} \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, crystallises from alcohol in four-sided prisms, melts at $206-207^{\circ}$ (corr.), dissolves in cold sulphuric and hydrochloric acids, is precipitated unchanged on dilution, and is converted by heating with aqueous potassium hydroxide into *a*-phenylhydantoin, $\text{CHPh} \cdot \begin{matrix} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} - \text{NH} \end{matrix}$. By passing hydrogen chloride into a hot alcoholic solution of the nitrile or amide, ethyl urethanophenylacetate, $\text{CO}_2\text{Et} \cdot \text{CHPh} \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, is produced (*Kossel, Abstr.*, 1892, 468), and from this the acid can be prepared by hydrolysing with potassium hydroxide, but melts at $119-121^{\circ}$ (corr.), and not at 155° as stated by Kossel. *Urethanophenylacetoxamidine*, $\text{CO}_2\text{Et} \cdot \text{NH} \cdot \text{CHPh} \cdot \text{C}(\text{NH}) \cdot \text{NH} \cdot \text{OH}$, prepared by

the action of hydroxylamine on the nitrile, crystallises from hot water in small prisms, sinters at 133° , and melts at 137° (corr.), forms a crystalline hydrochloride and hydrobromide, but has no basic properties and does not dissolve in cold dilute potassium or sodium hydroxide, but is decomposed, with liberation of hydroxylamine, when the mixture is heated; the *acetyl* derivative, $C_{13}H_{17}O_4N_3$, crystallises from alcohol and melts at 162° ; the oxamidine combines with cyanic acid to a compound, $C_{12}H_{16}O_4N_4$, which melts and liberates gas at 160° , has feeble basic properties, and forms a crystalline nitrate, hydrochloride, and sulphate; with phenylcarbimide, the oxamidine forms a compound, $C_{18}H_{20}O_4N_4$, which crystallises from alcohol in needles or prisms, melts at 183° , and has no basic properties. The oxamidine differs from Tiemann's amidoximes, $R \cdot C(NH_2) : NOH$, in that it has no basic properties and is not stable towards alkalis, and is therefore regarded as the isomeride, $NH : CR \cdot NH \cdot OH$.
T. M. L.

Dialkylamino-*o*-benzoylbenzoic Acids and their Derivatives. By ALBIN HALLER and ALFRED GUYOT (*Bull. Soc. Chim.*, 1901, [iii], 25, 165—174).—Mainly a summary of work already published (Abstr., 1894, i, 602; 1898, i, 670). *Benzylethylaminobenzoylbenzoic acid*, $C_7H_7 \cdot NEt \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot CO_2H$, prepared by the condensation of benzylethylaniline with phthalic anhydride in presence of aluminium chloride, forms pale yellow needles and melts at 172° .
N. L.

Dialkylaminobenzylbenzoic Acids derived from the Benzoyl Acids. II. By ALBIN HALLER and ALFRED GUYOT (*Bull. Soc. Chim.*, 1901, [iii], 25, 200—205).—Most of the results contained in this paper have been previously published (Abstr., 1898, i, 670). Dimethylaminobenzylbenzoic acid melts at 173° .

Benzylethylaminobenzylbenzoic acid forms small, colourless crystals melting at 145° . The *methyl* ester is an uncrystallisable liquid which gives a red violet coloration with lead peroxide.

Dimethylamino-*m*-hydroxybenzylbenzoic acid melts at 204° .

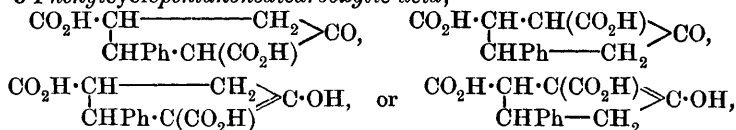
Diethylamino-m-hydroxybenzylbenzoic acid crystallises in colourless needles melting at 194° .
N. L.

Addition of Diethyl Succinate to $\alpha\beta$ -Unsaturated Ketones and Esters. By HANS STOBBE (*Annalen*, 1901, 315, 219—246. Compare this vol., i, 147).—[With RICHARD FISCHER].— *β -Phenylbutane- $\alpha\gamma\delta$ -tricarboxylic (β -phenyl-*n*-butanetricarboxylic) acid*,



prepared from diethyl succinate and ethyl cinnamate, separates from dilute aqueous solutions in lustrous, triclinic crystals, which begin to soften at 181° , and melt, evolving gas, at 199 — 200° ; the *calcium* and *barium* salts contain $2\frac{1}{2}H_2O$ and $5H_2O$ respectively, whilst the *silver* salt decomposes spontaneously even when protected from light. The *trimethyl* ester crystallises from petroleum in highly refractive prisms, and melts at 54 — 55° .

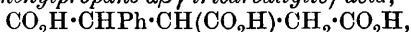
3-Phenylcyclopentanonedicarboxylic acid,



the methyl ester of which is obtained by the action of sodium methoxide on the foregoing methyl ester, has not been isolated, because sodium hydroxide regenerates β -phenylbutane- $\alpha\gamma$ -tricarboxylic acid; the *methyl* ester crystallises from petroleum or alcohol in white needles and melts at 94° . The *sodium* salt forms slender white needles, and the *copper* salt crystallises in pale green needles which contain 1 mol. of alcohol and melt at 145 — 147° ; the *semicarbazone* crystallises from alcohol and melts at 162 — 163° .

3-Phenylcyclopentanone-4-carboxylic acid, $\text{CO}_2\text{H} \cdot \underset{\text{CHPh} \cdot \text{CH}_2}{\text{CH} - \text{CH}_2} > \text{CO}$,

prepared from the methyl ester of the foregoing dicarboxylic acid by the action of hot 30 per cent. sulphuric acid, crystallises from hot water and melts at 117 — 118° ; the *silver* salt is indifferent towards light, and the *semicarbazide* derivative, $\text{C}_{12}\text{H}_{12}\text{ON}_2$, which is not the normal semicarbazone, melts and decomposes at 208° . When 3-phenylcyclopentanone-4-carboxylic acid is oxidised with nitric acid, α -phenyltricarballic (a-phenylpropane- $\alpha\beta\gamma$ -tricarballic) acid,



is produced; it crystallises from water, and melts at 199° , when it decomposes vigorously. M. O. F.

Constitution of the Oxime Hydrochlorides. By THOR EKECRANTZ (*Öfvers. Svenska Vetensk.-Akad. Förhandl.*, 1899, 56, 985—1002).—The author has studied the relations between α - and β -*p*-nitrobenzaloximes, their behaviour towards solvents, &c.

The α -oxime melts at 128.5 — 129° and separates from water in dark yellow, rhombic needles showing a deep blue colour when viewed parallel to the long direction of the crystals. The hydrochloride, when treated with sodium carbonate, yields the β -oxime, which separates from amyl alcohol in long, well-formed plates, showing strong double refraction and melting at 174 — 175° .

When determined in the ordinary way in capillary tubes, the melting points of the hydrochlorides of the α - and β -oximes are the same (about 112 — 117°), but when the salts are heated in test-tubes about 1.5 cm. wide, hydrogen chloride is copiously evolved, and fusion is not complete until a temperature of about 134° is reached, the two in this case also having the same melting point; on extracting the two tubes when cold, they are found to contain the α -oxime melting at 128.5 — 129° .

The action of various solvents on β -*p*-nitrobenzaloxime was examined, and it was found that alcohol and ethyl acetate effect a partial transformation into the α -modification.

On methylating the hydrochlorides of the two oximes by means of diazomethane, the methyl ester of the α -oxime is obtained in both cases. T. H. P.

[Condensation of] Benzaldehyde with Propaldehyde. By THEODOR HACKHOFFER (*Monatsh.*, 1901, 22, 95—108).—In presence of a concentrated solution of potassium carbonate, benzaldehyde and propaldehyde condense to an *aldol*, $\text{OH} \cdot \text{CHPh} \cdot \text{CHMe} \cdot \text{CHO}$, which breaks up into its components on all attempts at distillation. The

oxime, $C_{10}H_{13}O_2N$, forms white crystals melting at 100° . On reduction of the aldol by aluminium amalgam, a *dihydric alcohol*, $C_{10}H_{14}O_2$, is obtained as a thick yellow liquid, which boils at 171° under 14 mm. and at 280° under atmospheric pressure; the *diacetate*, $C_{10}H_{12}O_2Ac_2$, distils at 180 — 185° under 13 mm., and at 287 — 290° under atmospheric pressure. By the action of a concentrated solution of sodium acetate on the aldol, water is eliminated and β -phenyl- α -methylacetaldehyde is formed. When treated with sulphuric acid, the dihydric alcohol yields β -phenyl- α -methylpropaldehyde.

K. J. P. O.

Cyclic β -Diketones. II. By GEORGES LESER (*Bull. Soc. Chim.*, 1901, [iii], 25, 196—199. Compare Abstr., 1900, 1, 430).—The ketonic acid, $C_9H_{16}O_3$, obtained, as formerly described (*loc. cit.*), by the hydrolysis of acetylmethylcyclohexanone, yields β -methyladipic acid on oxidation with chromic acid, and has therefore the constitution $CH_2Ac \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CO_2H$, whilst the hexanone has the constitution $CHMe \cdot \begin{smallmatrix} CH_2 \cdot CO \\ CH_2 \cdot CH_2 \end{smallmatrix} \cdot CHAc$. The latter formula is in accord with the molecular refraction of the compound (found, 43.9; calculated, 43.7).

4-Acetyl-1:4-dimethyl-3-cyclohexanone, prepared by treating acetylmethylcyclohexanone with sodium and methyl iodide, is a colourless liquid which boils at 114 — 116° under 11 mm. pressure, has a mol. refraction 46.28 (calculated 46.39), and forms a crystalline monoxime melting at 122 — 123° ; it does not exhibit the characteristic reactions of β -diketones, since it gives no coloration with ferric chloride, does not form a copper salt, and is insoluble in alkalis. On treatment with dilute potash, it undergoes hydrolysis, partly into acetic acid and 1:4-dimethyl-3-cyclohexanone, partly with the formation of ζ -keto- β - ϵ -dimethyloctioic acid. The last is an oily liquid which boils at 181 — 182° under 12 mm. pressure, and forms a crystalline *silver* salt. 1:4-Dimethyl-3-cyclohexanone boils at 172 — 174° under 750 mm. pressure, and has a sp. gr. 0.9083 at 13° , $[\alpha]_D + 11.6^\circ$, and a mol. refraction 37.13 (calculated 37.01). It forms an *oxime* crystallising in silky needles melting at 97 — 98° , and a semicarbazone melting at 176 — 177° .

N. L.

Ketones of Wood Oil. Dimethylcyclohexenone. By AUGUSTE BÉHAL (*Compt. rend.*, 1901, 132, 342—345).—One of the series of ketones extracted by the author from wood tar (Abstr., 1899, i, 121) has the composition $C_8H_{12}O$, boils at 194° , forms an *oxime* melting at 102.5° and a benzoyl derivative melting at 129° , and when oxidised with potassium permanganate yields acetic and α -methylsuccinic acids. From these results, it is concluded that the ketone in question is a *dimethylcyclohexenone* of the constitution $CO \cdot \begin{smallmatrix} CHMe \cdot CH_2 \\ CH_2 \cdot CH \end{smallmatrix} \cdot CMe$, and hence, judging by analogy, the methylcyclohexenone previously described (Abstr., 1898, i, 403) has probably the constitution $CO \cdot \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH \end{smallmatrix} \cdot CMe$, and not $CO \cdot \begin{smallmatrix} CH_2 \cdot CMe \\ CH_2 \cdot CH_2 \end{smallmatrix} \cdot CH$, as formerly suggested.

According to Bischoff, α -methylsuccinic acid boils at 247 — 248° , but

the author finds that when distilled, even under diminished pressure, it loses water and yields a lactone which boils at 205—206° and has a sp. gr. 1.0588 at 0°.

N. L.

2-Hydroxybenzylacetophenone. By W. FEUERSTEIN and A. MUSCULUS (*Ber.*, 1901, 34, 409—412).—The 2-hydroxybenzylacetophenone obtained by Kostanecki and Feuerstein (*Abstr.*, 1898, i, 370) by the action of dilute acids on 2-hydroxybenzylidenediacetophenone, is converted by reduction with sodium amalgam into dihydrocoumaryl alcohol, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OH}$ (*Abstr.*, 1896, i, 302), and its constitution is thus proved.

2-Methoxybenzylacetophenone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COPh}$, is a viscid oil which boils at 223° under 20 mm. pressure. The *o*-nitrophenylhydrazone crystallises in orange-red needles melting at 120—121°.

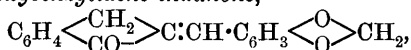
A. H.

Some Substituted Benzylideneindanones. By W. FEUERSTEIN (*Ber.*, 1901, 34, 412—415).—Indanone reacts with substituted aldehydes in the same manner as with benzaldehyde (*Kipping, Trans.*, 1894, 65,

428). *o*-Hydroxybenzylideneindanone, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CO}\end{smallmatrix}\right\rangle\text{C}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$,

crystallises in lustrous, yellow needles, which melt and decompose at 206°. *m*-Hydroxybenzylideneindanone crystallises in small, yellow prisms melting at 198—199°. *p*-Hydroxybenzylideneindanone crystallises in faintly yellow needles which melt at 219—220°. *mp*-Dihydroxy-

benzylideneindanone, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CO}\end{smallmatrix}\right\rangle\text{C}\cdot\text{CH}\cdot\text{C}_6\text{H}_3(\text{OH})_2$, prepared from protocatechuic aldehyde, crystallises in deep yellow needles melting at 255—256°; as a dye, it produces orange-yellow shades with an alumina mordant. *m*-Methoxy-*p*-hydroxybenzylideneindanone was prepared from vanillin, and forms microscopic, yellow crystals melting at 187°. *mp*-Methylenedioxybenzylidene indanone,



prepared from piperonal, crystallises in long, yellowish, lustrous needles and melts at 179—180°. *p*-Dimethylaminobenzylideneindanone forms golden, lustrous plates melting at 165—166°.

A. H.

Preparation and Properties of Dialkylaminoanthraquinones. III. By ALBIN HALLER and ALFRED GUYOT (*Bull. Soc. Chim.*, 1901, [iii], 25, 205—213. Compare *Abstr.*, 1898, i, 593).—The dialkylaminobenzylbenzoic acids (this vol., i, 276) are readily converted by the action of concentrated sulphuric acid into dialkylaminoanthranols, which, when oxidised with ferric chloride, yield successively the corresponding oxanthranols and anthraquinones.

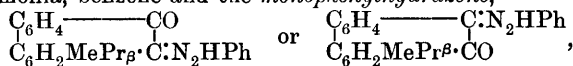
Diethylaminoanthraquinone, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_3\cdot\text{NEt}_2$, crystallises in red prisms, needles, or scales melting at 156°. Benzylethylaminoanthraquinone crystallises in large, red needles melting at 131°, and readily forms sulphonic derivatives, substitution probably occurring in the benzyl group. Diethylaminohydroxyanthraquinonesulphonic acid,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2(\text{OH})(\text{NEt}_2)\cdot\text{SO}_3\text{H}$, from diethylamino-*m*-hydroxybenzylbenzoic acid, crystallises in slender, bronze-coloured needles; the *barium*, *calcium*, and *magnesium* salts crystallise well. *Diethylamino-dihydroxyanthraquinone*, obtained by fusing the preceding compound with potash or soda at 200° , crystallises from toluene in large, violet-black needles, and from alcohol in red needles containing $1\text{H}_2\text{O}$. This compound does not dye with metallic mordants and is therefore concluded to be a quinizarin derivative, having the two hydroxyl groups in the meta-position with regard to each other. *Dimethylaminohydroxyanthraquinonesulphonic acid* is difficult to obtain in the pure state, and differs from the preceding compound in that it cannot be fused with potash without destruction of the NMe_2 group and in yielding a slaty black, crystalline precipitate with copper sulphate solution. N. L.

Action of Phenylhydrazine on Phenanthraquinone. By EUGEN BAMBERGER and JACOB GROB (*Ber.*, 1901, **34**, 533—539).—Phenylhydrazine reacts explosively with dry phenanthraquinone, but the action takes place quietly when ether is used as a solvent, nitrogen being evolved, and ammonia, benzene, and diphenyl formed, along with *phenanthroxazine*, $\begin{smallmatrix} \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{NH}\cdot\text{C}\cdot\text{C}_6\text{H}_4 \\ | \quad | \\ \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{O}\cdot\text{C}\cdot\text{C}_6\text{H}_4 \end{smallmatrix}$. The formation of the oxazine is probably due to the phenylhydrazine initially reducing the quinone to phenanthraquinol, the latter immediately combining with the ammonia produced to form the aminohydroxyphenanthrene, $\begin{smallmatrix} \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{NH}_2 \\ | \\ \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{OH} \end{smallmatrix}$, 2 mols. of which condense to yield the oxazine, with elimination of $2\text{H}_2\text{O}$. Phenanthroxazine crystallises from boiling nitrobenzene or naphthalene in slender, bronze-coloured needles with a metallic lustre, melts at $350\text{--}355^\circ$ (uncorr.), and sublimes at a higher temperature in reddish-brown scales; it is indifferent to acids and alkalis, and is not changed when boiled for several hours with acetic anhydride. In presence of zinc chloride, however, the anhydride gives rise after a few minutes to an *acetyl* derivative, which crystallises from amyl alcohol in slender, yellowish-white needles, and melts somewhat indefinitely at about 330° .

The constitution of phenanthroxazine follows from its yielding phenanthrazine when treated with gaseous ammonia in nitrobenzene solution at $130\text{--}140^\circ$; that it is formed from phenanthraquinone as just explained is shown by its production along with phenanthrazine when gaseous ammonia is passed into phenanthraquinol dissolved in cumene at $120\text{--}130^\circ$.

Retenequinone interacts with phenylhydrazine in ethereal solution to form ammonia, benzene and the *monophenylhydrazone*,



but fails to yield the expected reteneoxazine.

W. A. D.

New Preparation of Terpeneol. By P. GENVRESSE (*Compt. rend.*, 1901, **132**, 637—639. Compare *Abstr.*, 1900, i, 351).—When

a mixture of pinene, alcohol, and nitrous acid (purified from nitric acid) is left at the ordinary temperature, reaction slowly takes place, and at the end of two months about two-thirds of the pinene is transformed. By fractional distillation of the product, first with steam and then alone under reduced pressure, a liquid is obtained which is identical in its chemical and physical properties with terpineol; the yield is about 75 per cent. of the pinene transformed. The melting point of the nitrosochloride, which seems not to have been recorded, was found to be 83° . Australene, when similarly treated, yields *d*-terpineol. Limonene gave a negative result. N. L.

New Alcohol derived from Limonene. By P. GENVRESSE (*Compt. rend.*, 1901, 132, 414—416. Compare Abstr., 1900, i, 351).—*Limonenol*, $C_{10}H_{16}O$, produced by the action of nitrous fumes on *d*-limonene cooled by ice and salt, is separated from the crude product, after neutralisation with sodium carbonate, by distillation in steam, and finally separated from unaltered hydrocarbon by extraction with a concentrated solution of sodium salicylate, this solvent having the property of dissolving terpenoid alcohols, but not terpenes. The compound is a colourless liquid having an agreeable odour, differing from that of pinenol or limonene; it boils without decomposition at 135° under 15 mm. pressure and has $[\alpha]_D + 19^{\circ}21'$ at 17° , a sp. gr. 0.9669 at 18° , and $n_D 1.497$. Its molecular refraction deduced from experimental data is 45.99, which corresponds with the value 46.5 calculated from Brühl's constants, on the assumption that the compound contains two double linkings. This assumption is justified by the fact that the alcohol absorbs 2 mols. of bromine without the evolution of hydrogen bromide.

Limonenone, $C_{10}H_{14}O$, a colourless liquid having an agreeable odour, is prepared by oxidising the preceding compound with chromic acid mixture; at 20° , it has $[\alpha]_D + 16^{\circ}4'$, $n_D 1.487$, and a sp. gr. 0.9606 at 20° . The molecular refraction calculated from the refractive index is 44.858, and from Brühl's constants 45.16, assuming two double linkings.

Limonenoxime, $C_{10}H_{14}NOH$, produced by treating the preceding ketone with alcoholic solutions of hydroxylamine hydrochloride and potassium hydroxide, is purified by distillation in steam; it melts at 85.5° , but if, after allowing the fused mass to solidify, the melting point is redetermined, it is found to have fallen to 72° . Small quantities of the oxime result from the action of nitrous fumes on limonene. The compound seems to be identical with *l*-carvoxime, the melting point of the latter corresponding with the lower melting point of the former; the substances have the same $[\alpha]_D$, namely, $-39^{\circ}42'$, whilst the benzoyl and phenylcarbimide derivatives agree in properties melting at 95° and 133° respectively. G. T. M.

Observations on Oximes and their Reduction to the corresponding Amines. By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 45—48).—Contrary to the statement generally made, that camphoroxime has in solution a molecular weight twice as great as that required by its formula, the author finds that in freezing benzene the molecular weight varies from 202.1 to 279.7 for concentrations between the limits 3 and 0.07 per cent.

Nägeli (Abstr., 1883, 728) stated that camphoroxime is completely

stable towards concentrated hydrochloric acid at 100—120°. The author finds, however, that when heated with hydrochloric acid in a sealed tube for an hour at 120°, camphoroxime yields campholenic acid.

According to Leuckart and Bach (Abstr., 1887, 376), camphoroxime gives only small quantities of bornylamine when reduced with sodium in alcoholic solution. By gradually adding sodium to a solution of the oxime in alcohol, the author obtains a yield equal to 55 per cent. of the theoretical of bornylamine, with properties almost identical with those of the amine described by Leuckart and Bach.

By the reduction of diphenylnitromethane by tin and hydrochloric acid, and by the reduction of an alcoholic solution of benzophenone-oxime by means of sodium, identical specimens of benzhydrylamine were obtained with the boiling point 301—302° under 746 mm. pressure, this temperature being 288—289°, according to Leuckart and Bach (Abstr., 1886, 1023), and Michaelis and Linow (*Ber.*, 1893, 26, 2168). The sp. gr. of benzhydrylamine is 1.0635 at 21.5°/0°, and n_D 1.59631 at 21.5°, giving for the molecular refraction according to the Lorentz and Lorenz formula the value 58.57. Benzhydrylamine *nitrate*, melting at about 200°, *oxalate* melting at about 185—188°, and *aurichloride* melting at 152—154° are described.

T. H. P.

Fenchene and Camphene. By IWAN L. KONDAKOFF and EUGEN LUTSCHININ (*Chem. Zeit.*, 1901, 25, 131—133. Compare Abstr., 1900, i, 604).—The authors have isolated one of the two constituents of fenchene in a pure form. It boils at 140—141°, has a sp. gr. 0.8385 at 20°/20° [α]_D - 55°, and shows the properties of a reduced aromatic compound with a double linking in the ring. The isomeride probably has a double linking attached to a tertiary carbon atom in the side chain.

Fenchyl iodide, C₁₀H₁₇I, obtained by the action of a solution of hydrogen iodide saturated at - 20° on fenchyl alcohol at the ordinary temperature, boils at 120—123° under 23 mm. pressure, has a sp. gr. 1.4199 at 21°/4°, and a slight levorotation. On treatment with alcoholic potash, it yields a fenchene boiling at 148—158°, and having a sp. gr. 0.8519 at 22°/22° and [α]_D + 2°4' at 40°. Fenchene hydriodide, C₁₀H₁₇I, obtained from this hydrocarbon distills at 120—120.5° under 23 mm. pressure, has a sp. gr. 1.427 at 21°/4° and [α]_D + 42°57' at 40°; when treated with alcoholic potash, it gives a fenchene boiling at 143—150°, and of sp. gr. 0.8482 at 19°/4°, together with some unaltered hydriodide; the latter reacts with moist silver oxide, yielding solid fenchyl alcohol.

Camphene hydriodide, which should be identical with *isobornyl iodide*, forms colourless crystals melting at 48—55°, and when treated with alcoholic potash gives a camphene melting at 49°, and having [α]_D - 5°55', together with unaltered iodide. This iodide reacts with silver oxide, yielding camphene and probably borneol (compare Wagner, Abstr., 1900, i, 96, 554).

J. J. S.

Eucalyptus Oil containing 60 per cent. of Geranyl Acetate. By HENRY G. SMITH (*Chem. News*, 1901, 83, 5).—Fresh leaves and branchlets of *Eucalyptus Macarthuri* collected in October and distilled with steam yielded 0.112 per cent. of oil. The oil has a sp. gr. 0.9245

at 15°, a rotation of +3.6° in a 100 mm. tube, is soluble in 70 per cent. alcohol, and contains 60 per cent of geranyl acetate, 10.64 per cent. of free alcohol calculated as geraniol, as well as eudesmol, which crystallised from the fraction distilling between 266° and 282°.

D. A. L.

Empyreumatic Oil of Juniper. By CATHELINEAU and JEAN HAUSER (*Bull. Soc. Chim.*, 1901, [iii], 25, 247—250. Compare Abstr., 1899, i, 536, 711, and 1900, i, 510).—The results of the fractional distillation of that portion of empyreumatic oil of juniper which is insoluble in sodium hydroxide have already been given (Abstr., 1899, i, 536). The investigation of the chemical nature of the various fractions thus obtained is, however, unsatisfactory, neither have processes based on steam distillation and extraction led to the separation of any well characterised individual substances. N. L.

New Case of Chloroform of Crystallisation: Leprarin-Chloroform. By GEORG KASSNER (*Arch. Pharm.*, 1901, 239, 44—48).—Leprarin (Zopf, Abstr., 1897, i, 437), of which the correct composition is $C_{19}H_{18}O_9$, crystallises from chloroform with $1CHCl_3$. Other cases of chloroform of crystallisation are cited. C. F. B.

Polycystin, a Crystalline Carotin from Polycystis flos aquæ. By WILHELM ZOPF (*Chem. Centr.*, 1901, i, 466; from *Ber. bot. Ges.*, 18, 461—467).—Polycystin, a crystalline carotin, has been isolated from the alcoholic extract of *Polycystis flos aquæ*. It separates from its solution in ether as a red, crystalline mass formed of long, slender needles and broad, rhombic leaflets, and has a metallic lustre. Its solutions are not fluorescent. The spectra of the light petroleum, ether, alcohol, and chloroform solutions are described in the original paper; they do not show the chlorophyll spectrum, and are not identical with that of the carotin from the carrot or from solanorubin. Polycystin is a eucarotin, for it does not combine with alkalis or with alkaline earths. E. W. W.

Bilifuscin. By LEO R. VON ZUMBUSCH (*Zeit. physiol. Chem.*, 1901, 31, 446—459).—Bilifuscin has been isolated from human biliary calculi in the form of an almost black powder having the composition $C_{64}H_{96}O_{14}N_7$. It shows no trace of crystalline structure, dissolves sparingly in chloroform, methyl alcohol, amyl alcohol, or acetone, but fairly readily in acetic acid, naphthalene or dimethylaniline, and also in alkalis.

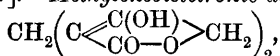
The nitrogen cannot be estimated by any of the ordinary modified Kjeldahl processes, and although numerous experiments have been made, it has not been settled in what form the nitrogen is evolved when bilifuscin is heated with fuming sulphuric acid. The pigment must certainly be very differently constituted from bilirubin. J. J. S.

Condensation Products of Tetronic Acid. By LUDWIG WOLFF (*Annalen*, 1901, 315, 145—173. Compare Abstr., 1900, i, 582).—

Tetronic acid, $\begin{matrix} CO \cdot CH_2 \\ CH_2 \cdot CO \end{matrix} > O$, undergoes condensation with aldehydes, ketones, and ketonic acids, surpassing acetoacetic and malonic esters in activity. The action has been studied in respect of formaldehyde

acetaldehyde, benzaldehyde, acetone, acetophenone, pyruvic acid, and diacetyl, and takes place without the assistance of a condensing agent; anhydrotetronic acid (Abstr., 1896, i, 524) also undergoes condensation with aldehydes, but α -substituted tetronic acids are indifferent.

[With W. SCHIMPF].—*Methylenebistetronic acid*,



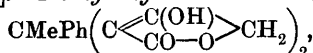
precipitated on mixing an aqueous solution of tetronic acid with formaldehyde, crystallises from a mixture of alcohol and petroleum in plates which melt and evolve gas at 245° ; the *calcium* salt contains $3\text{H}_2\text{O}$, and the *barium* salt crystallises from water in long needles.

Ethylidenebistetronic acid, $\text{CHMe}\left(\text{C} \begin{array}{c} \text{C(OH)} \\ \text{CO-O} \end{array} \text{CH}_2\right)_2$, crystallises from hot water in lustrous prisms, and after recrystallisation from a mixture of alcohol and petroleum melts at $209\text{--}210^\circ$, evolving gas; it is identical with the bye-product obtained on preparing tetronic acid from bromotetronic acid and a reducing agent (Abstr., 1896, i, 523). Like the foregoing substance, ethylidenebistetronic acid develops a red coloration with ferric chloride; hot aniline converts it into anilinetetronic acid, and sodium nitrite gives rise to oximinotetronic acid.

isopropylidenebistetronic acid, $\text{CMe}_2\left(\text{C} \begin{array}{c} \text{C(OH)} \\ \text{CO-O} \end{array} \text{CH}_2\right)_2$, crystallises in needles, and melts, decomposing, at $200\text{--}201^\circ$; it requires 50–60 parts of boiling alcohol to dissolve it, and on continued heating with the solvent is resolved into tetronic acid and the acid $\text{C}_{14}\text{H}_{16}\text{O}_6$ melting at 120° . The *dibenzoyl* derivative crystallises from alcohol in lustrous leaflets and melts at 162° . Phenylhydrazine converts *isopropylidenebistetronic acid* into the phenylhydrazone of tetronic acid, whilst aniline gives rise to the *anilide* of tetronic acid, $\text{NHPh} \cdot \text{C} \begin{array}{c} \text{CH}_2 \\ \text{CH} \cdot \text{CO} \end{array} \text{O}$,

which crystallises from alcohol in silky needles and melts at 220° . When *isopropylidenebistetronic acid* is heated with an aqueous solution of hydroxylamine hydrochloride, the compound $\text{C}_{11}\text{H}_{18}\text{O}_6\text{N}$ is produced, separating from alcohol in well-formed crystals which melt at 158° and immediately resolidify; the substance cannot be regarded as the normal oxime, because it does not develop colour with ferric chloride. The *dibromide*, $\text{CMe}_2\left(\text{CBr} \begin{array}{c} \text{CO} \\ \text{CO-O} \end{array} \text{CH}_2\right)_2$, prepared by the action of bromine on *isopropylidenebistetronic acid* dissolved in moist chloroform, crystallises from a mixture of petroleum and dry chloroform in lustrous prisms, and melts at 113° , when it decomposes; it is neutral towards sodium carbonate, and is slowly decomposed by hot water, yielding bromotetronic and bistetronic acids.

[With M. GABLER].—*Phenylethylidenebistetronic acid*,



prepared from acetophenone and tetronic acid, crystallises from alcohol and melts, evolving gas, at $169\text{--}171^\circ$.

Ketobutylidenebistetronic acid, $\text{COMe} \cdot \text{CMe}\left(\text{C} \begin{array}{c} \text{C(OH)} \\ \text{CO-O} \end{array} \text{CH}_2\right)_2$,

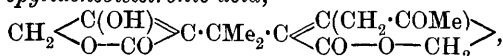
obtained from diacetyl and tetronic acid, crystallises from a mixture of benzene and methyl alcohol, and melts somewhat indefinitely at 144° , when it decomposes; the oxime crystallises in lustrous plates, which become yellow at 175° and decompose at about 208° .

Propiobistetronic acid, $\text{CO}_2\text{H}\cdot\text{CMe}(\text{C} \begin{smallmatrix} \text{C(OH)} \\ \text{CO-O} \end{smallmatrix} \text{CH}_2)_2$, derived from tetronic and pyruvic acids, crystallises in large, lustrous prisms containing $1\text{H}_2\text{O}$, and melts at 196° , when it decomposes.

The compound, $\text{C}_{18}\text{H}_{14}\text{O}_{10}$, produced on adding acetaldehyde to a cold concentrated aqueous solution of anhydrotetronic acid, crystallises in needles containing $3\text{H}_2\text{O}$, and melts at 120° ; the anhydrous compound melts and decomposes at 247° .

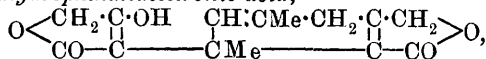
Tetronic acid undergoes condensation with mesityl oxide, yielding the acid, $\text{C}_{14}\text{H}_{16}\text{O}_6$, which crystallises from dilute alcohol in lustrous needles and melts, evolving gas, at 230° ; *ketohexyttetronic acid*, $\text{COMe}\cdot\text{CH}_2\cdot\text{CMe}_2\begin{smallmatrix} \text{C(OH)} \\ \text{CO-O} \end{smallmatrix}\text{CH}_2$, accompanies it, and crystallises from hot water in lustrous pyramids, which sinter at 120° and melt at $122-124^{\circ}$.

Acetonylpropylidenebistetronic acid,



prepared by the action of acetone on *isopropylidenebistetronic acid* in alcoholic, aqueous, or hydrochloric acid solution, crystallises from dilute alcohol in aggregates of small needles containing $1\text{H}_2\text{O}$, which is removed at 80° ; when dried in air, the substance sinters at 115° , melts, evolving gas at 120° , then resolidifies, and finally fuses at $162-163^{\circ}$, but after dehydration in a vacuum or at 80° , it becomes yellow at about 130° , and melts at $165-167^{\circ}$. The *benzoyl* derivative crystallises from alcohol in large, lustrous prisms, and melts at $134-135^{\circ}$; the *oxime* separates in four-sided, colourless plates, and melts, evolving gas, at 180° . The oxime reduces silver nitrate and Fehling's solutions, and is resolved by glacial acetic acid into tetronic acid, a nitrogenous compound which decomposes at 212° , and a base, $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$, which crystallises from hot alcohol in lustrous, white needles, and melts at $151-152^{\circ}$.

Dimethyldihydrophthalidetetronic acid,



prepared by heating acetonylpropylidenebistetronic acid with barium carbonate suspended in water, crystallises from alcohol in yellow plates or lustrous prisms, and melts at 250° , evolving gas; bromine converts it into the compound, $\text{C}_{14}\text{H}_{11}\text{O}_5\text{Br}$, which crystallises from a mixture of chloroform and petroleum in colourless prisms melting and decomposing at 178° .

M. O. F.

Coumarins from Phenol. By HANS VON PECHMANN and E. VON KRAFFT (*Ber.*, 1901, 34, 421-423).—4-Methylcoumarin is best prepared by treating a mixture of ethyl acetoacetate and phenol with cold concentrated sulphuric acid; the yield is never more than 3 per cent. The melting point of the pure product is $81-82^{\circ}$ (not $125-126^{\circ}$,

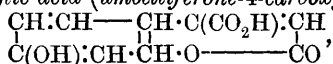
Pechmann and Duisberg, Abstr., 1884, 66). *Ethyl coumarin-4-carboxylate*, obtained by the condensation of phenol and ethyl oxalacetate by means of concentrated sulphuric acid, crystallises in slender, colourless needles melting at 77—78°, and when hydrolysed with alcoholic potash yields the corresponding *acid*, which crystallises in small needles and melts at 179—180°.

R. H. P.

Coumarins from 1:2:4-Trihydroxybenzene. By HANS VON PECHMANN and E. VON KRAFFT (*Ber.*, 1901, 34, 423—426).—1:2:4-Trihydroxybenzene, when condensed with ethyl acetoacetate by means of concentrated sulphuric acid or an alcoholic solution of zinc chloride, yields 4-methylæsculetin, which crystallises in small, yellowish, lustrous needles and melts at 269—270°. *Ethyl æsculetin-4-carboxylate*, formed from ethyl oxalacetate with 1:2:4-trihydroxybenzene, crystallises in yellow needles with $\frac{1}{2}$ H₂O, melts at 207—208° and, when hydrolysed, yields the corresponding *acid*, which crystallises with H₂O and melts at 295°. *Ethyl æsculetin-4-carboxylate*, when treated successively with potash and methyl iodide, forms the *dimethyl ether* of æsculetin-4-carboxylic acid; this crystallises in golden needles, melts at 241—244°, and forms a *silver salt*, which, when distilled with steam, yields æsculetin dimethyl ether. *Ethyl æsculetin-3-carboxylate*, obtained by the condensation of 2:3:5-trihydroxybenzaldehyde with ethyl malonate, crystallises in lustrous brown tablets, melts at 244—245°, and when hydrolysed yields the corresponding *acid*, crystallising in small, yellow needles and melting and decomposing at 270°.

R. H. P.

7-Hydroxycoumarin-4-carboxylic Acid. By HANS VON PECHMANN and ERDMANN GRAEGER (*Ber.*, 1901, 34, 378—386).—7-Hydroxycoumarone-4-carboxylic acid (*umbelliferone-4-carboxylic acid*),



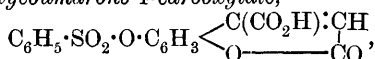
prepared by hydrolysing the ethyl ester, melts at 247—248°, separates from water in minute needles containing $1\frac{1}{2}$ H₂O, or in forms containing 2H₂O, and in alkaline solution shows a yellow colour and gradually develops a green fluorescence. The *ethyl ester*, C₁₂H₁₀O₅, prepared by the action of sodium ethoxide on an alcoholic solution of ethyl oxalacetate and resorcinol, crystallises from hot water or alcohol in yellow prisms with a greenish reflection, melts at 153—154°, and dissolves in alkalis; a red bye-product is described which becomes yellow at about 300°, and sublimes without melting. The *methyl ester*, prepared by condensing in methyl alcoholic solution, is less soluble than the ethyl ester, crystallises from dilute alcohol in greenish-yellow prisms, and melts at 178°.

7-Methoxycoumarone-4-carboxylic acid, C₁₁H₈O₅, prepared by hydrolysing its methyl ester, crystallises from hot water or alcohol in yellow needles, melts at 219°, and is converted into 7-methoxycoumarone by the dry distillation of the silver salt. The *methyl ester*, C₁₂H₁₀O₅, separates from wood-spirit as a yellow, crystalline powder and melts at 115°.

7-Acetoxycoumarone-4-carboxylic acid, C₁₂H₈O₆, crystallises from hot water in felted, silky needles, melts at 193°, and is converted by heat

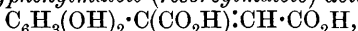
into 7-acetoxycoumarone; the *ethyl* ester, $C_{14}H_{12}O_6$, crystallises from dilute alcohol in white, felted needles and melts at $118-119^\circ$. *Ethyl 7-benzoyloxy coumarone-4-carboxylate*, $C_{19}H_{14}O_6$, crystallises from dilute alcohol in white needles and melts at 118° .

Methyl-7-p-bromobenzoyloxy coumarone-4-carboxylate, $C_{18}H_{11}O_6Br$, crystallises from dilute alcohol in white needles and melts at 98° . *Methyl-7-benzenesulphonoxy coumarone-4-carboxylate*,



crystallises from benzene in white prisms and melts at 171.5° .

β -2 : 4-Dihydroxyphenylmaleic (resorcylmaleic) acid,



prepared by the action of baryta on 7-hydroxycoumaronecarboxylic acid, melts and decomposes at $187-188^\circ$. *β -2 : 4-Diacetoxyphenylmaleic*

anhydride, $C_6H_3(\text{OAc})_2 \cdot \text{CH} \cdot \text{CO} \begin{array}{l} \text{CH} \cdot \text{CO} \\ \text{O} \end{array}$, crystallises in white needles and melts at $121-122^\circ$.

8-Bromo-7-hydroxycoumarone-4-carboxylic acid, $C_{10}H_5O_5Br$, crystallises from dilute alcohol in yellow needles and melts at 260° . The *ethyl* ester crystallises from alcohol or acetone in golden-yellow, felted needles and melts at 203° .

7-Hydroxycoumarone-3 carboxylic acid, $C_{10}H_6O_5$, separates from dilute alcohol as a colourless, crystalline powder, loses water at 105° , and melts at 262° , and, unlike the isomeride described above, is readily decomposed by heat into carbon dioxide and umbelliferone. The *ethyl* ester, $C_{12}H_{10}O_5$, prepared from resorcin aldehyde, malonic acid, and piperidine, crystallises from dilute alcohol in white, glistening needles or flakes, loses water at 100° , and melts at $165-170^\circ$. T. M. L.

Solubilities of Alkaloids in Carbon Tetrachloride. By IWAN SCHINDELMEISER (*Chem. Zeit.*, 1901, 25, 129) —The following numbers give the weights of alkaloids soluble in 100 parts of pure carbon tetrachloride at 17° . Morphine, 0.032; codeine, 1.328; papaverine, 0.203; narceine, 0.011; atropine, 1.136; cocaine, 18.503; strychnine, 0.645; brucine, 1.973. The alkaloids used were in all cases crystalline, and were previously finely ground and dried for 2 weeks over quicklime. J. J. S.

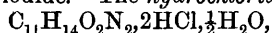
Hydrocinchonine. By ÉMILE JUNGFLEISCH and EUGÈNE LÉGER (*Compt. rend.*, 1901, 132, 410-412. Compare *ibid.*, 1869, 69, 284). —The authors now find that the base cinchonifine extracted by them from crude cinchonine by the action of dilute sulphuric acid is not isomeric but identical with hydrocinchonine obtained by oxidising the alkaloid with potassium permanganate. The two preparations have when pure, the same melting point, 278° (corr.), and specific rotation $198.6-199.5^\circ$; their double zinc chlorides are chemically and crystallographically identical. There is still some discrepancy between the sulphates, that obtained from hydrocinchonine by Skraup and also by Först and Böhringer is said to contain $12H_2O$, whilst the authors' preparation from cinchonifine crystallises with $2H_2O$ from concentrated, and with $11H_2O$ from dilute solutions; the hydrated salts containing 11 and $12H_2O$ appear, however, to be similar in crys-

talline form, solubility (1 in $30\text{H}_2\text{O}$), and melting point, 195° ; they are, moreover, both optically active in the solid state. G. T. M.

Corybulbine. By JOHANNES GADAMER and D. BRUNS (*Arch. Pharm.*, 1901, **239**, 39—44. Compare Dobbie, Lauder, and Paliatseas, *Trans.*, 1901, **79**, 87).—Corybulbine has $[\alpha]_D + 303.3^\circ$ at 20° in chloroform solution. Dehydrocorybulbine hydriodide was obtained crystallised with $1\text{H}_2\text{O}$, not 2 (Ziegenbein, *Abstr.*, 1897, i, 175); the base is reduced by zinc and sulphuric acid to *i-corybulbine*, which is optically inactive, and melted (it was perhaps impure) at 220° .

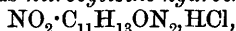
C. F. B.

Cytisine. By MARTIN FREUND and ADOLF FRIEDMANN (*Ber.*, 1901, **34**, 605—619).—Cytisine interacts with aqueous hydrogen peroxide at the ordinary temperature as a secondary base, the imino-group being converted into the *isonitroso*-group, $\text{N}\cdot\text{OH}$ (compare Mamlock and Wolfenstein, *Abstr.*, 1900, i, 209). The product of the action, *hydroxycytisine*, $\text{C}_{11}\text{H}_{13}\text{NO}\cdot\text{N}\cdot\text{OH}$, crystallises from water or alcohol, melts and decomposes at $223\text{—}226^\circ$, is not changed by boiling concentrated mineral acids or alkalis, and readily reduces warm ammoniacal silver nitrate or Fehling's solution; no definite product could be obtained by its oxidation with alkaline potassium permanganate, or on heating with methyl iodide at 100° . It is indifferent to phenylthiocarbimide, and does not liberate iodine from either neutral or acid solutions of potassium iodide. The *hydrochloride*,



forms rhombic octahedra and melts and decomposes at 270° , whilst the *platinichloride* does not melt at 325° ; the *nitrate*, with $1\text{H}_2\text{O}$, melts at $145\text{—}147^\circ$, the anhydrous salt melting at 100° . The *acetyl* derivative, $\text{C}_{11}\text{H}_{13}\text{NO}\cdot\text{N}\cdot\text{OAc}$, crystallises from water or alcoholic ether and melts at 117° . With aqueous sulphurous acid, *hydroxycytisine* yields the *sulphamic acid*, $\text{C}_{11}\text{H}_{13}\text{NO}\cdot\text{N}\cdot\text{SO}_3\text{H}\cdot 2\text{H}_2\text{O}$, which crystallises from water in stellate aggregates of needles, decomposes at 280° , and when boiled with hydrochloric acid is hydrolysed quantitatively to sulphuric acid and cytisine.

As stated by Partheil (*Abstr.*, 1891, **231**, 750) cytisine is converted by warm concentrated nitric acid into a *nitronitrosocytisine*, and the same substance is formed on slowly adding nitrosocytisine (von Buchka and Magalhaes, *Abstr.*, 1891, 750) to well-cooled fuming nitric acid; when heated with alcoholic hydrogen chloride at 100° , it loses the nitroso-group and yields *nitrocytisine hydrochloride*,



which crystallises from its concentrated aqueous solution, and decomposes at $270\text{—}280^\circ$. *Nitrocytisine*, $\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}_3$, crystallises from absolute alcohol in beautiful, yellow, rhombic prisms, melts at $185\text{—}188^\circ$, and combines with phenylthiocarbimide to form the *thiocarbamide*, $\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_4\text{S}$, which crystallises from nitrobenzene in yellow leaflets and melts and decomposes at $252\text{—}253^\circ$.

Acetylnitrocytisine, $\text{NO}_2\text{C}_{11}\text{H}_{12}\text{NO}\cdot\text{NAc}$, obtained either by the action of acetic anhydride on the nitro-base, or, in small yield only and in an impure state, by warming acetylcytisine with concentrated nitric acid of sp. gr. 1.4, crystallises from alcohol in lance-like needles

and melts at 223—225°. *Aminocytisine*, formed on reducing nitrocytisine with tin and hydrochloric acid, is a viscous oil; the *hydrochloride*, $C_{11}H_{15}ON_3 \cdot 2HCl$, crystallises from water on adding alcohol in stout, four-sided prisms, and melts at 305°. All attempts to convert aminocytisine into a hydroxycytisine through the diazo-reaction failed, ill-defined products only being formed.

Acetylaminocytisine, $NH_2 \cdot C_{11}H_{12}NO \cdot NAc$, obtained by carefully reducing nitroacetylcytisine in the cold with tin and hydrochloric acid, separates from chloroform on adding light petroleum, melts at 242—245°, and when boiled with hydrochloric acid yields aminocytisine hydrochloride; like aminocytisine, it yields no definite product on diazotisation.

As stated by Lammers (*Arch. Pharm.*, 1897, 235, 374), hydriodic acid at 180—190° does not act on cytisine; after heating for 4 hours at 225°, however, in presence of amorphous phosphorus, complete decomposition occurs, ammonia being formed along with a small quantity of a *base*, $C_{11}H_{14}ON_2$, which crystallises from alcohol in beautiful needles, softens at 182°, and melts at 187°; its salts are decomposed by water, but it can be heated with concentrated sulphuric acid or aqueous potassium hydroxide without change.

Cytisine condenses with aqueous formaldehyde at the ordinary temperature to form *methylenedicytisine*, $CH_2(C_{11}H_{13}ON_2)_2$, which crystallises best from toluene and melts at 212°. W. A. D.

Damascenine, a Constituent of the Seeds of Nigella Damascena. By HERBERT POMMERHNE (*Arch. Pharm.*, 1901, 239, 34—39).—A further account is given of the *isomeride* of damascenine, formed when the latter substance is heated with alcoholic potash (*Abstr.*, 1900, i, 684). It has the composition $C_9H_{11}O_3N \cdot 3H_2O$, melts at 76—77°, or at 140—141° when anhydrous, and has an acid as well as a basic character, neutralising 1NaOH. As stated already, the salts which it forms with acids are practically identical with those of damascenine itself. C. F. B.

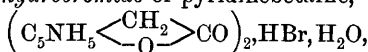
Compounds of Bismuth Chloride with Organic Bases. By LUDWIG VANINO and OTTO HAUSER (*Ber.*, 1901, 34, 416—420).—A solution of bismuth chloride in acetone is precipitated by aromatic bases. Many of these, however, such as aniline, methyl-, and dimethylaniline, and *o*- and *p*-toluidine do not yield simple compounds, whilst others yield definite crystalline derivatives.

Quinoline bismuth chloride, $C_9H_7N \cdot BiCl_3$, is a white, crystalline mass, which is only slowly decomposed by water and is not hygroscopic. If free hydrochloric acid be present, the salt, $(C_9H_7N \cdot HCl)_2 \cdot BiCl_3$, is also formed. *Quinoline bismuth iodide*, $C_9H_7N \cdot BiI_3$, is formed as a red crystalline powder when quinoline bismuth chloride is added to boiling aqueous potassium iodide. *Quinoline hydrochloride bismuth chloride*, $C_9H_7N \cdot HCl \cdot BiCl_3$, is prepared by dissolving quinoline bismuth chloride in hydrochloric acid and evaporating. *Pyridine bismuth chloride*, $(C_5H_5N)_3(BiCl_3)_2$, has already been described by Montemartini (this vol., i, 163). *Pyridine bismuth iodide* is a deep red powder, which is soluble both in alcohol and aqueous potassium iodide, and decomposes when heated without melting.

Pyridine hydrochloride bismuth chloride, $(C_5H_5N \cdot HCl)_3(BiCl_3)_2$, is produced when pyridine bismuth chloride is dissolved in hydrochloric acid, and crystallises in very soluble needles. *α -Naphthylamine bismuth chloride*, $(C_{10}H_7 \cdot NH_2)_2(BiCl_3)_3$, is a voluminous crystalline precipitate which is readily decomposed by water. *α -Naphthylamine bismuth iodide*, $(C_{10}H_7 \cdot NH_2)_2BiI_3$, crystallises in long, fascicular groups of deep red needles, and is decomposed by water. Bismuth chloride in acetone solution also gives precipitates with anhydroformaldehydeaniline and with cocaine.

A. H.

Action of Monohaloid Aliphatic Acids on Pyridine and Quinoline. By L. J. SIMON and L. DUBREUIL (*Compt. rend.*, 1901, 132, 418—421. Compare Krüger, *Abstr.*, 1890, 1431; 1891, 941, 1388).—The *basic hydrobromide* of pyridinebetaine,



produced by mixing monobromoacetic acid (2 mols.) and pyridine (3 mols.) in alcoholic solutions, separates in white crystals; quinoline behaves similarly, yielding the *hydrobromide*, $(C_{11}H_9NO)_2 \cdot HBr, H_2O$. The corresponding hydrochlorides of pyridine and quinoline betaines are formed in a similar manner and also crystallise with $1H_2O$.

This reaction has been extended to other monohaloid acids of the acetic series, and it is found that the action becomes less vigorous as the homologous series is ascended; the *hydrobromides* of the betaines, $C_5NH_5 \langle \begin{smallmatrix} CHMe \\ O \end{smallmatrix} \rangle CO$ and $C_5NH_5 \langle \begin{smallmatrix} CHEt \\ O \end{smallmatrix} \rangle CO$, have been obtained in this investigation.

When monobromosuccinic acid acts on the tertiary amine, the reaction takes a different course, hydrogen bromide is eliminated, and the salt of the corresponding unsaturated acid is formed; in the case of quinoline, a well-defined crystalline *quinoline fumarate* has been isolated.

G. T. M.

Nitrostilbazoles. By KARL FEIST (*Ber.*, 1901, 34, 464—467. Compare Baurath, *Abstr.*, 1888, 65 and 608; Roth, this vol., i, 165).—Nitrostilbazoles, $C_5NH_4 \cdot CH:CH \cdot C_6H_4 \cdot NO_2$, are formed when molecular quantities of 2-picoline and *o*-, *m*-, or *p*-nitrobenzaldehyde are heated for 6 hours at 220—225°, either with or without the addition of zinc chloride. The products are best isolated in the form of their sparingly soluble mercuric chlorides.

o-Nitrostilbazole crystallises from dilute alcohol in colourless needles melting at 95—96°; the *hydrochloride* melts and decomposes at 206—212°; the *aurichloride* is a sparingly soluble greyish-yellow amorphous precipitate, as is also the *platinichloride*, which melts and decomposes at 220—224°; the *dibromide*, $C_{13}H_{10}O_2N_2Br_2$, crystallises in colourless prisms melting at 167—168°.

m-Nitrostilbazole crystallises in yellowish plates melting at 127°; the *hydrochloride* forms glistening, yellow needles which slowly decompose at 200°; the *aurichloride* melts at 187°; the *platinichloride* melts and decomposes at 240°; and the *dibromide* forms prismatic needles melting at 153°.

p-Nitrostilbazole melts at 125—126° and readily turns red on ex-

posure to the air. The *hydrochloride* does not crystallise readily, and melts at 140—180°; the *mercurichloride*, $(C_{13}H_{19}O_2N_2, HCl)_2HgCl_2, H_2O$, crystallises in sparingly soluble, reddish-yellow needles melting at 195°; the *aurichloride* melts and decomposes at 205°; the *platinichloride* at 206—207°; and the *dibromide* forms pale-yellow crystals melting at 173°.

J. J. S.

Ecgonic Acid. By RICHARD WILLSTÄTTER and ADOLF BODE (*Ber.*, 1901, 34, 519—523).—*d*-Ecgonic acid obtained along with *d*-tropic acid by oxidising tropine with chromic acid in sulphuric acid solution, crystallises from ethyl acetate or benzene in colourless needles, melts at 93—95° (compare Liebermann, *Abstr.*, 1891, 749), and contains one methyl group attached to nitrogen. *l*-Ecgonic acid obtained similarly from *l*-ecgonine has the properties assigned to it by Liebermann, and also contains one methyl group; the *methyl ester*, $C_8H_{13}O_3N$, is colourless, boils at 275° under 13·5 mm. pressure, and does not react with phenylhydrazine or hydroxylamine. It does not yield a nitrosoamine or a benzoyl derivative, and is not changed by methyl iodide at the ordinary temperature. These facts are not in accord with Liebermann's formula for the acid, even when correction is made for recent views as to the true nature of tropine and ecgonine (*Abstr.*, 1898, i, 178). It is probable that ecgonic acid is a 1-*methylpyrrolidone-2-acetic acid*, $\begin{matrix} CO \cdot NMe \\ | \\ CH_2 \cdot CH_2 \end{matrix} > CH \cdot CH_2 \cdot CO_2H$.

W. A. D.

Nitroformaldehyde Phenylhydrazone. By EUGEN BAMBERGER and OTTO SCHMIDT (*Ber.*, 1901, 34, 574—594. Compare *Abstr.*, 1894, i, 183; 1900, i, 566).—Nitroformaldehyde phenylhydrazone, $NO_2 \cdot CH : N_2 \cdot HPh$, exists in two, presumably stereoisomeric, modifications. The α -compound crystallises from benzene, light petroleum, or chloroform and forms long, orange-red, glistening, monoclinic prisms melting at 74·5—75·5°. The β -isomeride crystallises from alcohol in small, golden-yellow needles melting at 84·5—85·5°, and is less readily soluble in most organic solvents. Either compound, when warmed with different solvents, is partially converted into its isomeride. Both phenylhydrazones react as pseudo-acids, and give rise to *sodium* salts, which are to be regarded as derived from the *isonitro*-compounds; they form orange-yellow, flat needles with a bronzy lustre. So far it has not been settled whether the two sodium derivatives are identical or not; when acted on by hydrochloric acid, they are immediately transformed into the normal nitro-compounds.

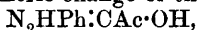
Nitroformazyl is obtained when the α -phenylhydrazone is kept for some three years, or when it is treated with potassium *isodiazobenzene*, or when either the α - or β -compound reacts with phenyldiazonium chloride or with almost any acid. Phenylformazyl (*Abstr.*, 1894, i, 183) is produced when an alkaline solution of normal diazobenzene acts on the α -phenylhydrazone.

A *methyl ether*, $OMe \cdot NO : CH : N : NHPh$, produced when either the α - or β -phenylhydrazone reacts with diazomethane in ethereal solution, forms dark, orange-red, glistening needles melting at 54·5°, and readily soluble in organic solvents. When kept for several days it decom-

poses, yielding a brown syrup; very dilute sulphuric acid converts it into formaldehyde and a compound, $\text{NPh}\cdot\text{N}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$.

A *N*-methyl ether, $\text{NMePh}\cdot\text{N}\cdot\text{CH}\cdot\text{NO}_2$, obtained by methylating the α - or β -sodium salt, crystallises from light petroleum in pale yellow, hair-like needles melting at $91-92^\circ$, and readily soluble in organic solvents but insoluble in alkalis; when reduced with zinc dust and acetic acid, it yields *as*-phenylmethylhydrazine, but when reduced with stannous chloride it also yields monomethylaniline and *phenylmethylhydrazidine*, $\text{NO}_2\cdot\text{CH}\cdot\text{N}\cdot\text{NMePh}$, which crystallises in flat needles melting at 101° ; with nitrous acid it gives a greenish-blue changing to blue coloration, and with ferric chloride, a pale green. The same ester may be obtained by the action of dibromonitromethane on *as*-phenylmethylhydrazine; other products formed at the same time are the *bromohydrazo*-compound, $\text{NMePh}\cdot\text{NH}\cdot\text{CHBr}\cdot\text{NO}_2$, melting at $98-100^\circ$, and pale yellow plates melting at $216-218^\circ$. J. J. S.

Acetylamidrazone. By EUGEN BAMBERGER and JACOB GROB (*Ber.*, 1901, 34, 539-548).—The following facts show that acetylamidrazone (Bamberger and Lorenzen, *Abstr.*, 1893, i, 157; Bamberger and de Gruyter, *Abstr.*, 1894, i, 98; Jagerspacher, *Abstr.*, 1895, i, 573) has the structure $\text{NH}_2\cdot\text{CAc}\cdot\text{N}\cdot\text{NHPh}$. With benzaldehyde, it yields the *benzylidene* derivative, $\text{CHPh}\cdot\text{N}\cdot\text{CAc}\cdot\text{N}\cdot\text{NHPh}$, which crystallises from alcohol in strongly refracting, orange-red prisms, softens at 156° and melts at $159-159.5^\circ$ (corr.). Formaldehyde gives rise to the analogous *methylene* derivative, $\text{CH}_2\cdot\text{N}\cdot\text{CAc}\cdot\text{N}\cdot\text{NHPh}$, which crystallises from light petroleum in orange needles, melts at $136-136.5^\circ$, and is apparently decomposed when crystallised from alcohol or acetone, the product melting at $180-190^\circ$. Nitrous acid at 0° converts acetylamidrazone into ammonia (1 mol.), and the tautomeric form, $\text{OH}\cdot\text{CAc}\cdot\text{N}\cdot\text{NPh}\cdot\text{NO}$, of *nitrosopyruvic acid phenylhydrazide*; this in aqueous-alcoholic solution reddens litmus, and dissolves readily in alkalis, including sodium carbonate and ammonia. It crystallises from ether in stellate aggregates of transparent prisms, softens at 78° , melts and decomposes at $85-85.5^\circ$, and slowly decomposes in the air; it is very sensitive to oxidising agents. It yields a *phenylhydrazone*, $\text{N}_2\text{HPh}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{NPh}\cdot\text{NO}$, which crystallises from chloroform on adding light petroleum in nearly white, silky needles, melting and decomposing at $123-129^\circ$ in a bath previously heated to $110-115^\circ$. The *p*-nitrophenylhydrazone is much more stable, and crystallises from boiling alcohol in beautiful, golden leaflets, which melt and decompose at $147-148^\circ$. When the hydrazide is warmed with hydrochloric acid, it yields the phenylhydrazone, $\text{N}_2\text{HPh}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$, of pyruvic acid, owing probably to the isomeric change of the compound,



initially formed; diazobenzene chloride, phenol, aniline, nitrosobenzene and, probably, diazobenzeneimide are formed as by-products.

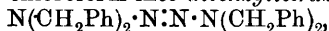
W. A. D.

Acid and Alcoholic Compounds of Phenylcarbazide or Phenylhydrazine Ureide. By PAUL CAZENEUVE (*Compt. rend.*, 1901, 132, 340-342).—Molecular compounds of phenylcarbazide with formic, acetic, propionic, *n*-butyric, valeric, and oxalic acids are obtained

by dissolving the carbazide in the acid or in a solution thereof, and cooling the solution obtained. They are crystalline substances which decompose when boiled with water, or when heated a little below 100° . Phenylcarbazide crystallises from its solutions in methyl, ethyl, *iso*-propyl, amyl, or benzyl alcohols with 1 mol. of the alcohol; these *compounds* are decomposed by water, and are less stable than the acid compounds. Phenylcarbazide also combines with phenols and with aldehydes. N. L.

Preparation of *as* Secondary Benzalhydrazines from Benzaldazines. By THEODOR CURTIUS and H. FRANZEN (*Ber.*, 1901, **34**, 552—559. Compare Abstr., 1900, i, 610).—2:4:5-Trimethylbenzaldazine may be reduced to the corresponding dibenzylamine by mixing it with zinc dust, and adding this in small portions to boiling alcohol alternately with a solution of glacial acetic acid in alcohol. *Di*-2:4:5-trimethylbenzylamine, $\text{NH}(\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Me}_3)_2$, crystallises in snow-white needles melting at 78° . The *sulphate* crystallises in small, white needles melting at 189° , the *hydrochloride* melts at 226° and the *nitrate* melts and decomposes at 203 — 204° . The *platinichloride* forms brownish-yellow plates. The *nitrite*, $\text{NH}(\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Me}_3)_2\cdot\text{HNO}_2$, crystallises in white needles which melt and decompose at 148° . When boiled for some time with alcohol, it yields the *nitrosoamine*, $\text{NO}\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Me}_3)_2$, which crystallises in spherical aggregates of faintly yellow coloured needles melting at 85° . On reduction with zinc dust and acetic acid in presence of alcohol at 10 — 15° , it yields *di*-2:4:5-trimethylbenzylhydrazine, $\text{NH}_2\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Me}_3)_2$, the *hydrochloride* of which crystallises in snow-white needles melting at about 203° . *Benzylidene-di*-2:4:5-trimethylbenzylhydrazine, $\text{CHPh}\cdot\text{N}\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Me}_3)_2$, forms matted, white needles melting at 119° .

Benzaldazine can readily be reduced by the method just described, yielding dibenzylamine, the *nitrite* of which crystallises in white plates and melts at 130° . Boiling alcohol converts it slowly into dibenzylnitrosoamine, which is reduced by zinc dust and acetic acid in presence of alcohol at the ordinary temperature, yielding *as*-dibenzylhydrazine, which has previously been prepared by Busch and Weiss (*Abstr.*, 1900, i, 699), who were, however, unable to obtain it in this way. Dibenzylhydrazine is converted by oxidation with mercuric oxide in presence of chloroform into *dibenzyltetrazone*,



which crystallises in needles melting at 97° .

A. H.

Preparation of Substituted Iminazoles [Glyoxalines]. By FRANZ KUNCKELL (*Ber.*, 1901, **34**, 637—642).—Substituted iminazoles can be prepared by the action of halogen-ketones on the amidines.

2:4-Diphenylglyoxaline, $\text{NH}\begin{matrix} \text{CPh}\cdot\text{N} \\ \text{CH}=\text{CPh} \end{matrix}$, prepared by the action of

bromoacetophenone on benzamidine, crystallises from alcohol in small, white needles, and melts at 193° . The *hydrochloride*, $\text{C}_{15}\text{H}_{13}\text{N}_2\text{Cl}$, dissolves in hot water and alcohol and melts at 264° . The *silver salt*, $\text{C}_{15}\text{H}_{11}\text{N}_2\text{Ag}$, forms a white, flocculent precipitate. Methyl and ethyl iodides, and bromoacetophenone form additive compounds with the

glyoxaline, which are converted into unstable ammonium bases by the action of alkalis or silver oxide, and then pass into 1-methyl, 1-ethyl, or 1-phenacyl-glyoxalines.

2-Phenyl-4-p-tolylglyoxaline, $\text{NH} \begin{smallmatrix} \text{CPh:N} \\ \text{CH}=\text{C} \cdot \text{C}_6\text{H}_4\text{Me} \end{smallmatrix}$, crystallises from benzene and melts at 183° . The isomeric 2:4-diphenyl-5-methylglyoxaline, $\text{NH} \begin{smallmatrix} \text{CPh:N} \\ \text{CMe} \cdot \text{CPh} \end{smallmatrix}$, prepared by the action of α -bromopropiophenone on benzamidine, melts at 215° ; the *hydrochloride* crystallises from alcohol in white needles and melts at 280° . The third isomeride, 4-phenyl-2-tolylglyoxaline, $\text{NH} \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_4\text{Me})\text{:N} \\ \text{CH}=\text{C} \cdot \text{CPh} \end{smallmatrix}$, is produced by the action of *p*-tolenylamidine on bromoacetophenone, but is not described.

By the action of α -bromoisobutyrophenone on benzamidine, *benzamidinoisobutyrophenone*, $\text{NH}:\text{CPh} \cdot \text{NH} \cdot \text{CMe}_2\text{Bz}$, is produced; it crystallises from dilute alcohol and melts at 175° ; the *phenylhydrazone*, $\text{C}_{23}\text{H}_{24}\text{N}_4$, crystallises from alcohol in yellow needles and melts at 110° . The fact that a glyoxaline is not formed in this case indicates that the condensation does not take place between the bromine atom and the imino-hydrogen to form (for example) $\text{CPh} \begin{smallmatrix} \text{N} \cdot \text{CH}_2 \\ \text{N} \cdot \text{CPh} \end{smallmatrix}$, as this should also take place with the dimethyl derivative; the formation of a silver salt also indicates that the product contains an imino-group.

Phenacylidenebenzamidine, $\text{NH}:\text{CPh} \cdot \text{N}:\text{CHBz}$, prepared by the action of dibromoacetophenone on benzamidine, crystallises from alcohol in white needles and melts at 224° . T. M. L.

Derivatives of 1-Phenyl-2:3-dimethyl-5-pyrazolone (Antipyrine). By GUSTAV EBERT and BAPTIST REUTER (*Chem. Zeit.*, 1901, 25, 43—44).—When aqueous solutions of phenyldimethylpyrazolone-trimethylammonium hydroxide, $\text{C}_8\text{H}_7\text{N}_2\text{Me}_2\text{PhO} \cdot \text{NMe}_3 \cdot \text{OH}$, are evaporated on the water-bath, or under reduced pressure, or are boiled with potassium hydroxide, the products formed are *acetyl-s-phenylmethylhydrazine* melting at 94° and betaine. *Diacetyl-s-phenylmethylhydrazine*, prepared by the action of acetic acid or anhydride on the monoacetyl compound, melts at 76 — 77° , but so far has not been converted into phenyldimethylpyrazolone.

The following salts of antipyrine have been prepared: the *acetylsalicylate* melting at 64 — 65° , *hydrogen camphorate* at 98 — 100° , and the *normal camphorate* at 95 — 98° .

4-Dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone *salicylate* melts at 69 — 70° , the *acetylsalicylate* at 66 — 70° , the *normal camphorate* at 81 — 82° , and the *hydrogen camphorate* at 94° . J. J. S.

Synthesis of Thymine and Other Uracils. By EMIL FISCHER and GEORG ROEDER (*Sitzungsber. Akad. Wiss. Berlin*, 1901, 12, 268—276).—Hydouracils may be produced either by the interaction of potassium cyanate and the salts of the esters of β -amino-acids, or by heating carbamide with an unsaturated acid; the second mode of syn-

thesis is preferable, since it obviates the necessity of preparing the amino-acid, and moreover the yield is better.

4-Methyldihydrouracil, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CHMe}$, obtained by the two new synthetical methods, and also by heating β -aminobutyric acid with carbamide, crystallises from water or alcohol in lustrous plates, and melts at $219\text{--}220^\circ$ (corr.); the yield from crotonic acid and carbamide is about 20 per cent. of the theoretical.

Ethyl β -aminobutyrate, prepared by esterifying a mixture of the corresponding acid with ethyl alcohol in the presence of hydrogen chloride, is a colourless liquid with an ammoniacal odour; it boils at $59\text{--}60^\circ$ under 12 mm. pressure, and mixes in all proportions with water, alcohol, ether, or light petroleum. When treated with potassium cyanate and dilute sulphuric acid, it yields the preceding compound.

The benzoyl derivative and phenylcarbimide of β -aminobutyric acid crystallise from hot water in needles, and melt respectively at 155° and 148° ; the latter substance, when heated with concentrated hydrochloric acid, yields a compound melting at 200° , which is probably a phenylmethyldihydrouracil.

Bromo-4-methyldihydrouracil, which contains the bromine atom either in position 4 or 5, is produced by heating 4-methyldihydrouracil at 100° with bromine and glacial acetic acid; it crystallises from alcohol in colourless needles and melts at $315\text{--}320^\circ$.

Methyluracil results from the action of a cold 15 per cent. solution of sodium hydroxide on the preceding compound; it melts at 320° and is identical with the product obtained by Gabriel from ethyl acetoacetate.

5-Methyldihydrouracil (hydrothymine), $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CHMe} \\ \text{CO} \text{—} \text{NH} \end{smallmatrix} \text{CH}_2$, obtained from carbamide and methylacrylic acid, separates from water or alcohol in small crystals melting at $264\text{--}265^\circ$ (corr.). This substance yields a bromo-derivative, which was employed in an impure state in the synthesis of thymine (5-methyluracil), $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CMe} \\ \text{CO} \text{—} \text{NH} \end{smallmatrix} \text{CH}$; the latter compound, when thus prepared, is identical with the natural product isolated from the thymus of the calf by Kossel and Neumann. Thymine sinters at 318° and melts at 321° . Dihydrouracil, produced from acrylic acid and carbamide, melts at 275° and crystallises in four-sided plates. This description tallies with that of Tafel's, and it was not found possible to obtain the compound in the form of needles as indicated by Weidel and Roithner (Abstr., 1896, i, 470).

G. T. M.

Synthesis of $\alpha\beta\gamma\delta$ -Tetraphenylpiperazine. By JULIUS SCHMIDT (Ber., 1901, 34, 627—629).—By reducing α - or β -diphenyldinitroethylene or α -diphenyldinitroethane with zinc dust and acetic acid, the hydrochloride of 2 : 3 : 5 : 6-tetraphenylpiperazine, $\text{NH} \begin{smallmatrix} \text{CHPh} \cdot \text{CHPh} \\ \text{CHPh} \cdot \text{CHPh} \end{smallmatrix} \text{NH}$, is produced; the base is a yellow oil; the hydrochloride, $\text{C}_{28}\text{H}_{28}\text{N}_2\text{Cl}_2$, crystallises from hot, strong hydrochloric acid in long, white needles, becomes brown at 249° , and melts at $254\text{--}256^\circ$; the platinichloride,

$C_{28}H_{26}N_2, H_2PtCl_6$, crystallises in golden-yellow, glistening flakes, and melts and decomposes vigorously at about 204° ; the aurichloride is not well characterised; the *picrate* crystallises in yellow needles and melts at $185-187^\circ$. T. M. L.

Absorption of Light by Indophenols. By PIERRE BAYRAC and CHARLES CAMICHEL (*Compt. rend.*, 1901, 132, 338-340. Compare Abstr., 1896, ii, 345, and this vol., i, 100).—The displacement of the absorption band in the red in the spectrum of indophenols containing a primary, instead of a tertiary, nitrogen atom in the para-position with regard to the nitrogen atom connecting the two nuclei may possibly occur, but is considered as not proved by the observations of Lemoult (this vol., i, 232). The authors find it impossible to define accurately the position of the extremities, and hence of the centre, of the band in the red. N. L.

Absorption Spectra of the Indophenols and of Dyes derived from Triphenylmethane. By CHARLES CAMICHEL and PIERRE BAYRAC (*Compt. rend.*, 1901, 132, 485-487).—The indophenols of thymol, *o*-cresol, and phenol, derived from *p*-diaminobenzene, and therefore containing primary nitrogen, are much less opaque in alcoholic solution than the corresponding compounds containing tertiary nitrogen, but like the latter show a broad absorption band with one edge in the red and the other in the infra-red, and do not agree with Lemoult's law of auxochromes (this vol., i, 232).

Among the dyes derived from triphenylmethane, malachite-green, methyl-green, and crystal violet show absorption bands with one edge only in the visible red, and in these cases also the law of auxochromes does not hold good. The substitution of primary nitrogen for tertiary nitrogen, and the number of tertiary nitrogen atoms in the molecule, are important factors in determining the action of the substance on light, but the true laws have still to be discovered. With alcoholic solutions of the indophenols and aqueous solutions of triphenylmethane derivatives, the coefficient of absorption is proportional to the concentration of the solution. C. H. B.

Action of Sodium Methoxide on Phenylnitroformaldehydephenylhydrazone, and the Oxidation of Benzaldehydephenylhydrazone. By EUGEN BAMBERGER and JACOB GROB (*Ber.*, 1901, 34, 523-532. Compare Abstr., 1899, i, 108).—Sodium methoxide reacts with phenylnitroformaldehydephenylhydrazone in methyl alcoholic solution to form benzoic acid and its methyl ester (about 30 per cent. of the total product), traces of benzanilide, and of a crystalline base melting at 109° , 1.5 per cent. of phenylformazyl (*Ber.*, 1894, 27, 158), and 39 per cent. of tetraphenyltetrazoline, $\begin{matrix} \text{CPh}\cdot\text{N}\cdot\text{NPh} \\ | \\ \text{NPh}\cdot\text{N}\cdot\text{CPh} \end{matrix}$; the

latter crystallises from a mixture of benzene and alcohol in long, amber-yellow or golden, lustrous needles, melts at $203-204^\circ$, and when distilled with zinc dust yields benzonitrile and aniline. Its constitution follows from its being formed by the oxidation of dehydrophenylbenzylidenehydrazine (Minuini and Rap, Abstr., 1897, i, 40) with sodium ethoxide and iodine, and as one of the products (about 8 per cent.)

obtained on subjecting benzaldehydephenylhydrazone to the same treatment (compare Ingle and Mann, *Trans.*, 1895, **67**, 606; von Pechmann, *Abstr.*, 1893, i, 461). On nitration in warm glacial acetic acid solution, it yields a *dinitro*-derivative, β -*dinitrotetraphenyltetrazoline*, which crystallises from xylene in short, lustrous, brownish-red needles, and melts when rapidly heated at 310° , and when slowly heated at 299° (uncorr.). An isomeric compound, α -*dinitrotetraphenyltetrazoline*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \text{CPh:N} \\ \text{N:CPh} \end{smallmatrix} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, is formed when phenylnitro-formaldehyde-*p*-nitrophenylhydrazone, $\text{NO}_2 \cdot \text{CPh:N}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, reacts with sodium methoxide in methyl alcoholic solution; it crystallises from xylene in slender, red needles and does not melt at 300° .

W. A. D.

Diphenylcarbodiiazide. By PAUL CAZENEUVE (*Compt. rend.*, 1901, **132**, 412—414. Compare *Abstr.*, 1900, i, 465).—Diphenylcarbodiiazide is conveniently prepared by slowly adding a hot alcoholic solution of diphenylcarbazine (1 mol.) to a boiling aqueous solution of silver acetate (4 mols.), filtering off the precipitated silver, evaporating the filtrate to dryness, extracting the residue with methyl alcohol, and precipitating the colourless crystalline product by means of ether. The compound is soluble in hot water or the alcohols, and crystallises in lustrous, acicular lamellæ; it does not melt but decomposes violently at temperatures below 100° . Unlike its generator, diphenylcarbodiiazide, it does not react with copper and mercury salts; when boiled with alcoholic alkali hydroxides, the solution assumes an orange tint owing to the formation of the alkali derivative of diphenylcarbazon. The acids of the acetic series dissolve diphenylcarbodiiazide, and the solutions rapidly become solid owing to the formation of molecular compounds. These substances resemble diphenylcarbodiiazide in their properties and are dissociated by heat; the formic acid compound may be considered to have the formula $\text{NPh:N} \cdot \text{CO} \cdot \text{N:NHP} \cdot \text{O} \cdot \text{CHO}$.

The *dibromide*, $\text{NPh:N} \cdot \text{CO} \cdot \text{NBr} \cdot \text{NBrPh}$, produced by the direct addition of bromine, separates from alcohol in pale yellow crystals darkening at 60° ; when boiled with alcoholic potassium hydroxide, it yields diphenylcarbazon and potassium bromide.

G. T. M.

Compounds of Proteids with Aldehydes. By LEO SCHWARZ (*Zeit. physiol. Chem.*, 1901, **31**, 460—478. Compare Benedicenti, *Arch. physiol.*, 1897, 219).—Crystallised serum-albumin combines with formaldehyde, yielding a substance which is no longer coagulated on heating; it is precipitated from its solution by ammonium sulphate even when only partially saturated. The precipitate is not so readily soluble as the original albumin, and is not thrown down from its solutions by the aid of 96 per cent., or even of absolute, alcohol. When precipitated by a mixture of alcohol and ether, it is at first soluble in water, but after some time becomes insoluble. The behaviour of the product towards various reagents has been studied. Analyses have also been made, but these show that the composition varies with the length of time during which the formaldehyde is allowed to remain in contact with the albumin.

Acetaldehyde, propaldehyde, and to a certain extent heptaldehyde,

behave similarly, but *isobutaldehyde* and *isovaleraldehyde* do not interfere with the coagulation of albumin. Benzaldehyde and salicylaldehyde give emulsions with serum-albumin solutions and no coagulation occurs on warming.

When a salt, for example, ammonium sulphate, is present, the aldehydo-compounds are much more readily precipitated.

Formaldehyde reacts in a similar manner with egg-albumin, serum-globulin, edestin, and heteroalbumose, but not with the iodo-derivative of egg-albumin.

In all cases, the number of aldehyde molecules added varies considerably with the length of time and probably with the aldehyde or proteid substance employed.

The aldehydo-compounds appear to be completely indifferent towards trypsin, and are only very slowly digested by pepsin.

J. J. S.

Gluco-proteid of Bone. By P. B. HAWK and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1900, xv—xvi).—In its reactions, the mucin of bone (osseo-mucoid) is the same as Mörner's chondro-mucoid from cartilage. The average analysis of what are regarded as the purest of the seven specimens prepared comes out much the same as that given by Mörner; there is, however, rather more hydrogen and oxygen in the osseo-mucoid.

W. D. H.

Iodohæmoglobin. By D. KURAÉEFF (*Zeit. physiol. Chem.*, 1901, 31, 527—542. Compare Abstr., 1898, i, 609; 1899, i, 314).—Oxyhæmoglobin has been converted into an iodo-derivative by the action of a solution of iodine in potassium iodide either in the presence of sodium hydrogen carbonate or of potassium iodate; when the latter method is employed, the product appears to be more readily soluble in alkali. *Iodohæmoglobin* (11·02—12·5 per cent. of iodine) forms a dark coloured precipitate which dries to a solid mass with a glistening, black fracture and when ground forms a brownish-black powder. The crude product is almost insoluble in alcohol or dilute acids, and its alkaline solutions give no precipitate with calcium hydroxide, but with barium hydroxide a substance is deposited which appears to have all the properties of iodohæmoglobin. After purification by the aid of sodium hydroxide, it dissolves in all alkalis, and even in dilute (0·5 per cent.) hydrochloric acid; the acid solution gives an absorption spectrum which appears to be identical with that given by an acid solution of hæmatin or of methæmoglobin. Experiments have been made on the action of pepsin salts and of trypsin on iodohæmoglobin.

Crystallised hæmin gives rises to an iodo-derivative containing 14·31 per cent. of iodine; it is readily soluble in alkalis or in alcohol containing a few drops of sulphuric acid, and is not so readily precipitated as iodohæmoglobin by ammonium sulphate from its alkaline solutions.

J. J. S.

Constitution of the Hæmatic Acids. By WILLIAM KÜSTER (*Annalen*, 1901, 315, 174—218. Compare this vol., i, 58).—The imide of tribasic hæmatic acid, $C_8H_5O_4N$, obtained by oxidising hæmatin with chromic acid, crystallises from hot water in aggregates of colourless needles, and from ether in monoclinic, holohedral crystals [$a : b : c = 0·5808 : 1 : 0·7138$;

$\beta = 87^{\circ}44'0''$]; it is very readily soluble in water, alcohol, ether, or chloroform, melts at $113.5-114.5^{\circ}$, is optically inactive, and has the electrical conductivity $K\ 0.00366$ at 25° . The ammonium salt melts at 100° and decomposes at 170° , the calcium salt contains $1H_2O$, the zinc salt separates from ether in monoclinic, holohedral crystals, and the cadmium, mercury, silver, and hydrogen silver salts are also crystalline.

The conversion of the foregoing imide into the anhydride of tribasic hæmatic acid is effected, not only by sodium hydroxide, but also under the influence of sodium carbonate, magnesium hydroxide, ammonium hydroxide, 50 per cent. sulphuric acid, and hydrogen bromide at 130° . The anhydride melts at $96-97^{\circ}$, and crystallises from ether in the rhombic system [$a:b:c = 0.533:1:?$]. It dissolves with some difficulty in chloroform or benzene, but readily in alcohol, ether, or glacial acetic acid; it is optically inactive, and has the electrical conductivity $K\ 0.0229$. The potassium, ammonium, strontium, barium, and silver salts have been analysed.

The remaining portions of the paper have been already noticed (*loc. cit.*), and the introductory part contains an exhaustive summary of previous work.

M. O. F.

Nucleohiston. By IVAR BANG (*Zeit. physiol. Chem.*, 1901, 31, 407—410). By ALBRECHT KOSSEL (*ibid.*, 410).—A continuation of the controversy between these authors (compare this vol., i, 57).

J. J. S.

Guanlyic Acid. By IVAR BANG (*Zeit. physiol. Chem.*, 1901, 31, 411—427. Compare Abstr., 1899, i, 179).—When guanlyic acid is hydrolysed by the aid of mineral acids, it yields guanine, glycerol, a pentose, and phosphoric acid according to the equation $C_{44}H_{66}O_{34}N_{20}P_4 + 10H_2O = 4C_5H_5ON_5 + 3C_5H_{10}O_5 + 3C_3H_8O_3 + 4H_3PO_4$. This composition for the acid is supported by analyses of it and of its silver salt, and a constitutional formula is also proposed; the glycerol is probably contained in the form of glycerophosphoric acid, and guanlyic acid is thus related to the lecithins, but bears no close relationship to inosinic acid as Kossel suggests.

J. J. S.

Nucleic Acids. By ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1901, 31, 428—431).—A polemical reply to Bang (compare preceding abstract).

J. J. S.

Composition of Nucleic Acids. By P. A. LEVENE (*Proc. Amer. Physiol. Soc.*, 1900, viii—ix. Compare Abstr., 1900, i, 572).—Two varieties of paranucleic acid gave very similar results on analysis:

| | C. | H. | N. | P. |
|----------------------|-------|------|-------|-------|
| From vitellin | 32.31 | 5.58 | 13.13 | 9.88 |
| From ichthulin | 32.56 | 6.00 | 14.00 | 10.34 |

Nucleic acids from different sources gave more divergent results:

| | C. | N. | N. | P ₂ O ₅ |
|---------------------|-------|------|-------|-------------------------------|
| From pancreas | 36.50 | 4.69 | 16.70 | 20.16 |
| „ codfish sperm ... | 36.73 | 5.12 | 16.78 | 20.47 |
| „ tubercle bacilli | 33.78 | 6.32 | 9.42 | 29.40 |

The acid obtained from pancreas contains adenine in addition to guanylic acid. In the preparation of nucleic acid, glycogen is precipitated simultaneously. The two can be separated by copper chloride; the copper salt of nucleic acid is insoluble, that of glycogen soluble in water.

W. D. H.

Paranucleic Acid. By P. A. LEVENE and C. ALSBERG (*Zeit. physiol. Chem.*, 1901, **31**, 543—555. Compare Abstr., 1900, ii, 555).—Vitellin is the name given by the authors to the paranucleo-compounds in yolk of egg, and the acid which may be obtained from this is called *avivitellie acid*. The copper salt has been prepared and analysed; it contains 12.36 per cent. of copper; the composition varies, however, slightly in different specimens. The acid is insoluble in water, alcohol, ether, or dilute acids, but dissolves in solutions of acetates, especially ammonium acetate. The salts of the alkalis are soluble, but those of the alkaline earths insoluble, in water. The sodium and potassium salts become insoluble in water when left in contact with alcohol. All specimens of the acid give Millon's reaction, but this may be due to an impurity. When hydrolysed with hydrochloric acid, it gives melanin, arginine, histidine, and probably lysine. The proteid part of the molecule is not a protamine, but the acid is probably an ester of albumin with phosphoric acid.

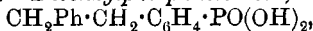
J. J. S.

Aromatic Chlorophosphines and their Derivatives. By AUGUST MICHAELIS (*Annalen*, 1901, **315**, 43—103. Compare Abstr., 1897, i, 48).—[With PAUL GÜSEWELL].—*Diphenylmethanechlorophosphine*, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{PCl}_2$, prepared from diphenylmethane, phosphorus trichloride, and aluminium chloride, is a colourless, viscous liquid which boils at 221° under 20 mm. pressure, and has a sp. gr. 1.182 at 17° ; the tetrachloride melts at 80° , and the oxychloride, $\text{C}_{13}\text{H}_{11}\cdot\text{POCl}_2$, boils at 261° under 20 mm. pressure, and has a sp. gr. 1.207. *Diphenylmethane-phosphinous acid*, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{PHO}\cdot\text{OH}$, is sparingly soluble in hot water, and when crystallised from alcohol melts at 84° ; the sodium, potassium, ammonium, barium, copper, and lead salts have been analysed, and the phenylhydrazine salt melts at 171° . *Diphenylmethanephosphinic acid*, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{PO}(\text{OH})_2$, crystallises in long, silky, colourless needles, and melts at 196° ; the hydrogen potassium, ammonium, barium, hydrogen barium, cobalt, copper, lead, and silver salts have been analysed, and the phenylhydrazine salt melts at 187° . *Phosphindiphenylmethane*, $\text{C}_{13}\text{H}_{11}\cdot\text{PO}_2$, is a snow-white, crystalline powder which melts at 169° ; water converts it slowly into the phosphinic acid. *Diphenylmethane phosphine*, $\text{C}_{13}\text{H}_{11}\cdot\text{PH}_2$, melts at 46° and boils at 184° under 20 mm. pressure; the hydriodide melts at 134° , and the dimethyl and diethyl derivatives boil at 197° and 235° under 20 mm. pressure respectively.

Benzophenonephosphinic acid, $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{PO}(\text{OH})_2$, obtained by oxidising diphenylmethanephosphinic acid with potassium permanganate, crystallises in white, nacreous leaflets and melts at 204° ; the silver, ammonium, and lead salts have been analysed, whilst the phenylhydrazone forms white, lustrous leaflets which melt at 124° . The diethyl ester of benzophenonephosphinic acid is a viscous oil having a pleasant odour; the oxime crystallises from absolute alcohol. Di-

phenyldichloromethaneoxychlorophosphine, $\text{CCl}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{POCl}_2$, prepared by the action of phosphorus pentachloride on benzophenonephosphinic acid, melts at 64° , and boils at 258° under 15 mm. pressure; it dissolves readily in ether, and is decomposed by water into benzophosphinic acid and hydrogen chloride.

[With HUGO CIANI].—*Dibenzylchlorophosphine*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{PCl}_2$, obtained from dibenzyl, phosphorus trichloride, and aluminium chloride, melts at 2° , and boils at 250° under 60 mm. pressure; the *tetrachloride* and *oxychloride* melt at 65° and 75° respectively. *Dibenzylphosphinous acid*, $\text{C}_{14}\text{H}_{13}\cdot\text{PHO}\cdot\text{OH}$, crystallises from dilute alcohol in transparent, nacreous leaflets, and melts at $156\text{--}157^\circ$; the *sodium* salt is sparingly soluble, and the *potassium*, *ammonium*, *lead*, *copper*, and *phenylhydrazine* salts are well defined. *Dibenzylphosphinic acid*,

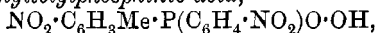


crystallises in lustrous, colourless leaflets, and melts at 256° ; when strongly heated, the acid is resolved into dibenzyl and metaphosphoric acid, whilst oxidation converts it into benzoic and *p*-benzophosphinic acids. *Dibenzylphosphine*, $\text{C}_{14}\text{H}_{13}\cdot\text{PH}_2$, melts at 75° , and boils at 190° under 45 mm. pressure; the hydriodide is crystalline, and the alkyl derivatives are oils.

[With A. BUSS].—*Diphenylchlorophosphine*, $\text{C}_6\text{H}_4\text{Ph}\cdot\text{PCl}_2$, prepared by heating diphenyl with phosphorus trichloride and aluminium chloride and distilling the product in an apparatus which is described and figured in the paper, melts at 5° , and boils at $200\text{--}220^\circ$; it has a sp. gr. 1.3098 at 14° . *Diphenylphosphinous acid*, $\text{C}_6\text{H}_4\text{Ph}\cdot\text{PHO}\cdot\text{OH}$, is a white, crystalline powder, forming well defined *potassium*, *calcium*, and *barium* salts.

[With WILHELM SÖCHTIG].—*Phenyl-p-tolylchlorophosphine*,
 $\text{C}_6\text{H}_4\text{Me}\cdot\text{PPhCl}$,

prepared by heating mercury diphenyl with tolylchlorophosphine in a reflux apparatus at 270° , is a colourless oil which has an unpleasant smell, and boils at 340° . The *trichloride*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{PPhCl}_3$, forms yellow crystals, and *phenyltolylphosphinic acid*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{PPhO}\cdot\text{OH}$, crystallises in slender needles melting at 116° , and forming well-defined salts. *Dinitrophenyltolylphosphinic acid*,



crystallises from alcohol in small, yellow needles and melts at 205° ; the *silver* salt is colourless. *Phenyltolylethylphosphine*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{PPhEt}$, a colourless oil having an agreeable odour, boils at 340° ; the *platini-chloride* forms pale yellow needles. *Phenyltolylmethylethylphosphonium iodide* crystallises in long, slender needles and melts at 138° ; the *platinichloride* crystallises in yellow needles. The *anilide* of phenyltolylphosphinous acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{PPh}\cdot\text{NHPh}$, obtained from phenyltolylchlorophosphine and aniline in benzene solution, crystallises from dilute alcohol in slender needles, and melts at 124° ; the *p-toluidide* melts at 142° .

p-Ditolylchlorophosphine, $(\text{C}_6\text{H}_4\text{Me})_2\text{PCl}$, is a colourless oil which boils at $345\text{--}350^\circ$; the *trichloride*, $(\text{C}_6\text{H}_4\text{Me})_2\text{PCl}_3$, is crystalline, and the *oxychloride*, $(\text{C}_6\text{H}_4\text{Me})_2\text{POCl}$, boils above 360° . *p-Ditolylphosphinic acid*, $(\text{C}_6\text{H}_4\text{Me})_2\text{PO}\cdot\text{OH}$, crystallises from dilute alcohol in slender, colourless needles and melts at 135° ; the *barium*, *lead*, *copper*,

silver, and phenylhydrazine salts are well defined. *Dinitroditolylphosphinic acid*, $(\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me})_2\text{PO} \cdot \text{OH}$, crystallises from alcohol in small, yellow needles, and melts at 194° . *p-Tolylbenzophosphinic acid*, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{P}(\text{C}_6\text{H}_4\text{Me})\text{O} \cdot \text{OH}$, prepared by oxidising ditolylphosphinic acid, forms a white, crystalline powder, which melts above 300° , and decomposes at higher temperatures into toluene, carbon, benzoic acid, and phosphoric acid.

[With PAUL SCHÖNHERR].—*Ditolylthiochlorophosphine*,



obtained by the action of aluminium chloride on a mixture of toluene and phosphorus thiochloride, crystallises from glacial acetic acid in short, white needles, and melts at 96° ; when heated with water at 130 — 140° , it yields the *anhydride* of ditolylxythiophosphinic acid, $[\text{PS}(\text{C}_6\text{H}_4\text{Me})_2]_2\text{O}$, which separates from alcohol in lustrous crystals melting at 165 — 166° . *Ditolylthiophosphinamide*, $\text{PS}(\text{C}_6\text{H}_4\text{Me})_2 \cdot \text{NH}_2$, separates from alcohol in hard, transparent crystals, and melts at 139° ; the *anilide*, *phenylhydrazide*, *piperidide*, and *diethylamide*, melt at 152° , 135.5° , 134° , and 177 — 178° respectively. *Ethyl ditolylthiophosphinate*, $\text{PS}(\text{C}_6\text{H}_4\text{Me})_2 \cdot \text{OEt}$, melts at 41 — 42° ; the *phenyl ester*, $\text{PS}(\text{C}_6\text{H}_4\text{Me})_2 \cdot \text{OPh}$, separates from alcohol in small crystals, and melts at 135° . *Ditolylmethylphosphine*, $\text{PMe}(\text{C}_6\text{H}_4\text{Me})_2$, is a colourless liquid which boils at 345° , and has a disagreeable odour.

Tolylbenzylphosphinic acid, $\text{C}_6\text{H}_4\text{Me} \cdot \text{P}(\text{CH}_2\text{Ph})\text{O} \cdot \text{OH}$, prepared by heating tolyldiphenol-o-phosphine with benzyl chloride at 170° , crystallises from alcohol in white, silky needles, and melts at 145° ; the *phenyl ester* forms small, white crystals and melts at 120° .

[With H. HESS].—*Di-ψ-cumylchlorophosphine*, $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{PCl}$, has not been obtained quite free from the primary derivative. *Phenyl-ψ-cumylchlorophosphine*, $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{PPhCl}$, boils at 208° and 356° under 10 mm. and atmospheric pressures respectively; the *trichloride*, $\text{C}_{15}\text{H}_{16} \cdot \text{PCl}_3$, forms small, yellow crystals, and the *oxychloride*, $\text{C}_{15}\text{H}_{16} \cdot \text{POCl}$, is a liquid which boils at 210 — 215° under 10 mm. pressure. *Phenyl-ψ-cumylphosphinic acid*, $\text{C}_{15}\text{H}_{16} \cdot \text{PO} \cdot \text{OH}$, crystallises from alcohol in needles melting at 181° ; the *phenylhydrazine salt* melts at 140.5° , and the *silver*, *copper*, and *cobalt* salts are well-defined. *Phenyltrinitro-ψ-cumylphosphinic acid*, $\text{C}_{15}\text{H}_{13}(\text{NO}_2)_3 \cdot \text{PO} \cdot \text{OH}$, crystallises in yellow prisms and melts at 197 — 198° ; the *silver salt* is amorphous. *Phenyl-ψ-cumylethylphosphine*, $\text{C}_{15}\text{H}_{16} \cdot \text{PEt}$, is a pale yellow, viscous liquid, which has a disagreeable smell, and boils at 225 — 230° and 352° under 10 mm. and atmospheric pressures respectively; the *mercurichloride* and *platinichloride* are crystalline, but the *methiodide* is an oil, forming a *platinichloride* which melts at 186° .

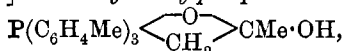
[With FELIX OHM].—*Tri-p-tolylphosphine*, $\text{P}(\text{C}_6\text{H}_4\text{Me})_3$, prepared by the action of sodium on a mixture of *p*-bromotoluene and phosphorus trichloride in ether, crystallises from alcohol in white prisms and melts at 146° . *Tri-p-tolylphosphine oxide*, $\text{PO}(\text{C}_6\text{H}_4\text{Me})_3$, obtained by oxidising the phosphine with sodium hypobromite, crystallises in small needles and melts at 145° ; the *trinitro-derivative* separates from alcohol in pale yellow needles and melts at 153° , whilst the *tri-amino-derivative* crystallises in aggregates of small needles containing 1 mol. of alcohol and melts at 235° .

Tri-p-tolylphosphine sulphide, $\text{PS}(\text{C}_6\text{H}_4\text{Me})_3$, crystallises from alcohol in white, lustrous needles and melts at 182° . *Tri-p-tolylphosphine selenide*, $(\text{C}_6\text{H}_4\text{Me})_3\text{PSe}$, separates from alcohol in snow-white, silky needles, and melts at 193° . *Tri-p-tolylmethylphosphonium iodide*, $\text{PMe}(\text{C}_6\text{H}_4\text{Me})_3\text{I}$, crystallises from water in needles containing $1\text{H}_2\text{O}$, and from alcohol in prisms containing 1 mol. of the solvent; it melts at 108° . The *chloride* melts at 80° , and the *platinichloride* crystallises in reddish-yellow needles melting at 245° .

Di-p-tolylmethylphosphine oxide, $\text{PMe}(\text{C}_6\text{H}_4\text{Me})_2\text{O}$, obtained by heating tritolylmethylphosphonium iodide with potassium hydroxide, crystallises from alcohol and melts at 143° . *Tri-p-tolylethylphosphonium iodide*, $\text{PEt}(\text{C}_6\text{H}_4\text{Me})_3\text{I}$, crystallises from water or from alcohol in white, lustrous needles, and melts at 185° . *Tri-p-tolyl-n-propylphosphonium iodide*, $\text{PPr}^n(\text{C}_6\text{H}_4\text{Me})_3\text{I}$, forms white needles and melts at 182° ; *tri-p-tolyl-isopropylphosphonium iodide* and *tri-p-tolylisobutylphosphonium iodide* melt at 184° and 104° respectively.

[With C. HOSSEUS].—*Ethyl tritolylphosphorbetaine hydrochloride*, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{P}(\text{C}_6\text{H}_4\text{Me})_3$, is prepared by heating tritolylphosphine with ethyl chloroacetate at 70° (compare Michaelis and Köhler, Abstr., 1899, i, 596); sodium carbonate or hydroxide converts the salt into *tritolylphosphorbetaine*, $\text{P}(\text{C}_6\text{H}_4\text{Me})_3\langle\text{O}\rangle_{\text{CH}_2}\text{CO}$, which separates from ether in small, white crystals and melts at 145° .

[With W. KRAHE].—*Tritolylmethylphosphorbetaine*,



crystallises from dilute alcohol in lustrous needles and melts at 107° . The *hydrochloride*, prepared by heating tritolylphosphine and chloroacetone at 85° , crystallises in aggregates of needles and melts at 245° ; the *platinichloride*, *aurichloride*, *hydrobromide*, and *hydriodide* melt at 220° , 164° , 210° , and 189° respectively.

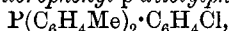
Phenyltritolylphosphorbetaine, $\text{P}(\text{C}_6\text{H}_4\text{Me})_3\langle\text{O}\rangle_{\text{CH}_2}\text{CPh}\cdot\text{OH}$, crystallises in aggregates of lustrous needles and melts at 177° . The *hydrochloride*, or *tritolylphenacylphosphonium chloride*, prepared from tritolylphosphine and chloroacetophenone, melts at 226° ; the *platinichloride*, *aurichloride*, *hydrobromide*, and *hydriodide*, melt at 240° , 156° , 248° , and 236° respectively.

Tolylmethyldiethylphosphorbetaine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{PEt}_2\langle\text{O}\rangle_{\text{CH}_2}\text{CMe}\cdot\text{OH}$, is very hygroscopic, and melts at 75° . The *hydrochloride*, obtained from diethyltolylphosphine and chloroacetone, is an oil, but the *platinichloride* and *picrate* melt at 178° and 127° respectively.

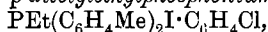
Phenyltolylmethyldiethylphosphorbetaine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{PEt}_2\langle\text{O}\rangle_{\text{CH}_2}\text{CPh}\cdot\text{OH}$, is a colourless oil; the *hydrochloride* is also an oil, but the *platinichloride* crystallises in small, reddish-yellow needles, and melts at 173° .

[With FELIX OHM].—*Tribenzophosphinic acid*, $\text{PO}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_3$, prepared by oxidising tritolylphosphine with chromic acid in acetic acid, forms a white, crystalline powder which melts at 247° , and sublimes when carefully heated; the *silver* salt is colourless.

[With L. EIFLER].—*Chlorophenyl-p-ditolylphosphine*,



produced by the action of sodium on an ethereal mixture of *p*-bromotoluene and chlorophenylchlorophosphine, separates from alcohol in colourless, highly refractive crystals melting at 115° . *Chlorophenyl-p-ditolylphosphine oxide*, $\text{PO}(\text{C}_6\text{H}_4\text{Me})_2 \cdot \text{C}_6\text{H}_4\text{Cl}$, crystallises from a mixture of benzene and petroleum in long, white needles and melts at 130° . *Chlorophenyl-p-ditolylphosphinesulphide*, $\text{PS}(\text{C}_6\text{H}_4\text{Me})_2 \cdot \text{C}_6\text{H}_4\text{Cl}$ and *chlorophenyl-p-ditolylphosphineselenide*, $\text{PSe}(\text{C}_6\text{H}_4\text{Me})_2 \cdot \text{C}_6\text{H}_4\text{Cl}$, melt at 149° and 172° respectively. *Chlorophenyl-p-ditolylmethylphosphonium iodide*, $\text{PMe}(\text{C}_6\text{H}_4\text{Me})_2 \cdot \text{I} \cdot \text{C}_6\text{H}_4\text{Cl}$, crystallises from water in long, broad needles containing $1\text{H}_2\text{O}$, and melts at 135° ; the *chloride* crystallises with $4\text{H}_2\text{O}$, and melts at 72° , and the *platinichloride* melts and decomposes at 235° . *Chlorophenyl-p-ditolyethylphosphonium iodide*,



forms needles which melt at 176.5° , and *chlorophenyl-p-ditolybenzylphosphonium iodide*, $\text{P}(\text{C}_6\text{H}_4\text{Me})_2(\text{CH}_2\text{Ph})\text{Cl} \cdot \text{C}_6\text{H}_4\text{Cl}$, crystallises in leaflets which contain $2\text{H}_2\text{O}$ and melt at 257° .

Chlorophenyldibenzophosphinic acid, $\text{PO}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2 \cdot \text{C}_6\text{H}_4\text{Cl}$, obtained on oxidising ditolylchlorophenylphosphine oxide with chromic acid in acetic acid, crystallises in white leaflets.

[With M. HEINE].—*m-Trixylylphosphine*, $\text{P}(\text{C}_6\text{H}_3\text{Me}_2)_3$, crystallises from alcohol in lustrous, white needles, and melts at 154° ; the *mercurichloride* decomposes without fusion at 270° , and the *sulphide* crystallises in lustrous prisms melting at 167° . *m-Trixylylmethylphosphonium iodide*, *m-trixylylethylphosphonium iodide*, and *m-trixylylethylphosphonium platinichloride* melt at 230.5° , 225° , and 252° respectively.

[With ALFRED SCHAEUBLE].—*p-Trixylylphosphine*, $\text{P}(\text{C}_6\text{H}_3\text{Me}_2)_3$, crystallises from absolute alcohol in small, white, lustrous needles, and melts at 155° ; the *mercurichloride* melts at 256° , whilst the *oxide* and *sulphide* melt at 173° and 170° respectively. *p-Trixylylmethylphosphonium iodide* and *p-trixylylethylphosphonium iodide* melt at 169° and 220° respectively.

[With D. VON KARCHOWSKI].—*Tri-ψ-cumylphosphine*, $\text{P}(\text{C}_6\text{H}_2\text{Me}_3)_3$, crystallises from a mixture of chloroform and petroleum in lustrous needles, and melts at $216\text{--}217^\circ$; the *oxide* and *sulphide* melt at 222° and 192° respectively. *Tri-ψ-cumylmethylphosphonium iodide* crystallises from alcohol in glistening leaflets and melts at 291° .

[With PAUL LOEBNER].—*Trimesitylphosphine*, $\text{P}(\text{C}_6\text{H}_2\text{Me}_3)_3$, separates as a white, crystalline powder, and melts at $205\text{--}206^\circ$. *Trimesitylmethylphosphonium iodide* melts at 269° .
M. O. F.

Organic Chemistry.

Action of Aluminium Bromide on Chlorinated Acyclic Hydrocarbons. By CHARLES POURRET (*Bull. Soc. Chim.*, 1901, [iii], 25, 293—299).—The preparation of bromine derivatives of methane by the action of aluminium bromide on the corresponding chlorine derivatives has already been described (*Abstr.*, 1900, i, 369). The present paper describes the application of the method to the preparation of ethyl bromide, ethylene dibromide, ethylidene dibromide, acetylene tetrabromide, and pentabromoethane. In the action of aluminium bromide on ethyl chloride, a little ethylene is formed, but hydrogen bromide is not evolved. From this, and from the fact that ethyl bromide is scarcely acted on by aluminium chloride or bromide, it is concluded that the reaction consists in a simple substitution of bromine for chlorine, and not in the formation of ethylene and the fixation of hydrogen bromide by the latter. N. L.

Abnormal Behaviour of Polyhaloid Compounds with Alcoholic Potash. By IWAN L. KONDAKOFF (*J. pr. Chem.*, 1901, [ii], 63, 113—140. Compare *Abstr.*, 1899, i, 556, and this vol., i, 62).—The author combats the explanation given by Nef, Faworsky, and others of the syntheses effected by aluminium chloride, zinc chloride, &c., and maintains that the known additive products of hydrocarbons with aluminium chloride, &c., and not the methylene derivatives suggested by Nef, are the intermediate products in these reactions.

In the apparently abnormal behaviour of polyhaloid compounds with alcoholic potash, the author does not consider, with Nef, that a direct elimination of halogen occurs with the formation of methylene or acetylidene ($\text{CH}_2\text{:C:}$) derivatives, but rather holds that complicated reactions take place, in which the alcohol or potassium ethoxide in the alcoholic potash plays a part. Thus, in the conversion of tetramethylethylene dibromide into tetramethylethylene, hydrogen bromide is first eliminated in the normal manner, and diisopropenyl produced. The latter now unites with ethyl alcohol forming a compound $\text{CMe}_2\text{Br}\cdot\text{CMe}_2\cdot\text{OEt}$, which then decomposes into ethyl hypobromite and tetramethylethylene. K. J. P. O.

Action of Zinc on Tetramethylene Dibromide and Diiodide. By JULES HAMONET (*Compt. rend.*, 1901, 132, 789—791).—The action of $\alpha\delta$ -dibromobutane or $\alpha\delta$ -diiodobutane on zinc in presence of alcohol yields butane, and not tetramethylene, and with zinc in the absence of alcohol, the product is ethylene. C. H. B.

Action of Zinc Dust on the Dibromides $\text{C}_n\text{H}_{2n}\text{Br}_2$. By WLADIMIR IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 151—154).—The action of zinc dust on $\alpha\gamma$ -dibromo- γ -methylbutane yields γ -methyl- α -butene, together with an unsaturated bromide, $\text{C}_5\text{H}_9\text{Br}$, an unsaturated ethyl ether, $\text{OEt}\cdot\text{C}_5\text{H}_9$, and probably oxy- $\alpha\gamma$ -dihydroxy γ -methylbutane. T. H. P.

Hexyl Bromide. By F. BODROUX (*Bull. Soc. Chim.*, 1901, [iii], 25, 299—300).—A claim for priority as against Mouneyrat. N. L.

Chlorine Derivatives of the Hydrocarbons in California Petroleum. By CHARLES F. MABERY and OTTO J. SIEPLEIN (*Amer. Chem. J.*, 1901, 25, 284—297. Compare Abstr., 1900, i, 533).—Chlorohexamethylene boils at 125.5°, and has the sp. gr. 0.9239 at 20°/4°, 0.9143 at 30°/4°, and 0.9044 at 40°/4°.

Chlorodimethylpentamethylene (?) distils at 147° and has a sp. gr. 0.9316 at 20°/4°. *Chloromethylhexamethylene* boils at 141—142°, and has a sp. gr. 0.9310 at 20°, the corresponding *nitrile* has a sp. gr. 0.9253 at 20°. When the chloro-derivative is treated with metallic sodium, a small amount of an unsaturated hydrocarbon boiling at 97°, with a double linking between a carbon atom of the side chain and one in the nucleus, is obtained. The *dibromide*, $C_7H_{12}Br_2$, derived from this has a sp. gr. 1.648 at 20°.

Chlorodimethylhexamethylene, $C_8H_{15}Cl$, boils at 168—170° and has a sp. gr. 0.9358 at 20°; the chlorine is probably contained in a side chain.

Chlorotrimethylhexamethylene, $C_9H_{17}Cl$, boils at 186—188° and has a sp. gr. 0.938 at 20°. When treated with sodium and dry ether, it yields an unsaturated *hydrocarbon*, C_9H_{16} , distilling at 135—140° and having a sp. gr. 0.7762 at 20°.

Chlorodecanaphthene, $C_{10}H_{19}Cl$, boils at 105—110° under 50 mm. pressure, and has a sp. gr. 0.947 at 20°. *Chloroundecanaphthene*, $C_{11}H_{21}Cl$, distils at 125—130° under 35 mm. pressure and has a sp. gr. 0.9583 at 20°. *Chlorododecanaphthene*, $C_{12}H_{23}Cl$, distils at 130—135° under 17 mm. pressure, and has a sp. gr. 0.9616 at 20°. *Chlorotridecanaphthene*, $C_{13}H_{25}Cl$, distils at 140—145° under 17 mm. pressure, and has a sp. gr. 0.9747 at 20°. *Chlorotetradecanaphthene*, $C_{14}H_{27}Cl$, distils at 150—155° under 13 mm. pressure, and has a sp. gr. 0.9748 at 20°/20°. *Chloropentadecanaphthene*, $C_{15}H_{29}Cl$, distils at 170—175° under 14 mm. pressure, and has a sp. gr. 0.9771 at 20°/20°.

All these chlorine derivatives have been obtained from the different hydrocarbons fractionated from California oils by passing chlorine into the oil floating on water. J. J. S.

Specific Gravities of Solutions of Three Substances: Alcohol, Ether, and Water. By W. I. BUSNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 128—143).—The author has determined the sp. gr. at 15°/15° of a number of different mixtures of alcohol, ether, and water. On comparing the numbers obtained with those given by Squibb (*Zeit. anal. Chem.*, 1887, 26), it is found that if one part of water be introduced into 100 parts of a mixture of alcohol and ether in any proportion, the sp. gr. of the mixture will be increased by about 0.002, the limiting numbers for the different mixtures being 0.001819 and 0.002334. On the basis of these observations, the following method is suggested for determining the composition of a mixture of alcohol, ether, and water. Firstly, the specific gravity is determined, after which the water present is completely removed by means of fused potassium hydroxide, and the sp. gr. of the resulting mixture of alcohol and ether also determined. The latter value, by reference to Squibb's

table (*loc. cit.*) gives the proportions of ether and alcohol, whilst the difference between the sp. gr. before and after dehydration, divided by 0.002, gives the quantity of water referred to 100 parts of the ether-alcohol mixture.

Attention is called to the fact that mixtures of these three liquids which are saturated with respect to water have approximately molecular composition. Two such mixtures were examined, their compositions corresponding very nearly with the formulæ: $2\text{EtOH} + 4\text{Et}_2\text{O} + 3\text{H}_2\text{O}$ and $2\text{EtOH} + 5\text{Et}_2\text{O} + 3\text{H}_2\text{O}$. T. H. P.

Action of Octyl Alcohol on its Sodium Derivative. Synthesis of Di- and Tri-caprylic Alcohols. By MARCEL GUERBET (*Compt. rend.*, 1901, 132, 685—688. Compare Abstr., 1899, i, 471, 472, and this vol., i, 182).—The condensation taking place between the higher primary alcohols and their sodium derivatives also occurs in the case of the secondary alcohols. Octylic alcohol, when heated in contact with its sodium derivative at 200—250°, undergoes condensation, yielding two new alcohols and a trace of heptioic acid, the formation of the acid being accompanied by an evolution of hydrogen.

Diocetyl alcohol, separated from the other products by fractional distillation, is a colourless liquid having an odour resembling that of suet, it boils at 173° under 17 mm. pressure, and has the sp. gr. 0.8473 at 0° and 0.8387 at 15°.

Triocetyl alcohol, purified by conversion into its phthalic ester, is a colourless, oily liquid boiling at 227—230° under 12 mm. pressure; its *acetic ester* boils at 224—227° under 10 mm. pressure. These compounds, like octyl alcohol itself, are both secondary alcohols, the esterification velocity of the dioctyl derivative being 20; amyl and heptyl alcohols give rise to primary alcohols, and these results indicate that in every case the condensation does not affect the carbon atom combined with the hydroxyl group. G. T. M.

Vaporisation and Hydration of Ethylene Glycol. By ROBERT DE FORCRAND (*Compt. rend.*, 1901, 132, 688—690. Compare this vol., ii, 224).—The boiling points of ethylene glycol under varying pressures have been determined, and the data obtained employed in calculating the molecular heat of vaporisation at different temperatures, this quantity decreases slowly from 14.60 Cal. at 130.6° to 12.06 Cal. at 197°, the boiling point of the substance under 760 mm. pressure. The calculated vapour pressure of the glycol is 13.34 mm. at 100°, and 0.026 mm. at 10°. The compound is excessively hygroscopic, and in six weeks it absorbs 60 per cent. of water, this amount corresponding with the formation of the hydrate, $\text{C}_2\text{H}_6\text{O}_2 \cdot 2\text{H}_2\text{O}$. The existence of this hydrate is also demonstrated thermochemically. The mean heat of hydration of glycol itself is 1.675 Cal., and it is found that the heats of hydration of mixtures of this substance with water, from $\text{C}_2\text{H}_6\text{O} \cdot 0.25\text{H}_2\text{O}$ to $\text{C}_2\text{H}_6\text{O} \cdot 2\text{H}_2\text{O}$, slowly decrease in accordance with the law expressed by the equation $Q = 1.675 - 0.260n$, but beyond this point they agree with the expression $Q = 1.202 - 0.147(n - 2)$, 1.202 being the heat of hydration of the dihydrate, and n the number of mols. of water. The following densities have been determined, $\text{C}_2\text{H}_6\text{O}_2$,

1.1297; $C_2H_6O_2 \cdot H_2O$, 1.17; $C_2H_6O_2 \cdot 2H_2O$, 1.53, and $C_2H_6O_2 \cdot 2.5H_2O$, 1.38, these data indicating that the formation of the dihydrate corresponds with the point of maximum contraction. The heat of formation of the dihydrate is 0.60 Cal. G. T. M.

Ethyl Hydroperoxide. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1901, **34**, 738—749. Compare this vol., i, 62).—*Ethyl hydroperoxide*, $EtO \cdot OH$, produced by shaking together a mixture of diethyl sulphate and excess of a 10 per cent. solution of hydrogen peroxide, is separated in the form of an oil by repeated distillation under ordinary and diminished pressures. The substance has not been obtained quite pure on account of its explosive nature; the product containing 80 per cent. of the compound boils at $47-49^\circ$ under 100 mm., and at $95-100^\circ$ under the ordinary pressure. It explodes when heated above its boiling point, or when mixed with "molecular" silver at the ordinary temperature; it has, however, no reducing action on silver oxide, and therefore differs from hydrogen peroxide, which reacts with silver oxide, but not with the finely divided metal.

Ethyl hydroperoxide is an acid the strength of which is comparable with that of phenol. The *sodium* and *potassium* salts show no tendency to crystallise, the *calcium* salt separates in readily soluble leaflets, the *barium* salt, $(C_2H_5O_2)_2Ba \cdot 2H_2O$, crystallises from water in lustrous prisms and from dilute alcohol in needles; it explodes on heating or by percussion, and is completely decomposed by carbon dioxide. Although the barium salt differs from barium peroxide in being readily soluble in water, yet it resembles the latter closely in other respects, and the authors accordingly assume that the compounds have constitutions corresponding with $Ba(O \cdot OEt)_2$ and $Ba(O \cdot O)_2Ba$ respectively. Ethyl hydroperoxide does not form salts with magnesia or with the hydroxides of the heavy metals; lead hydroxide, however, behaves exceptionally in yielding a white, unstable compound which rapidly becomes yellow. The reaction between "molecular" silver and ethyl hydroperoxide is moderated by the presence of water, and a dilute solution of the peroxide yields ethyl alcohol, acetaldehyde, alcohol, and oxygen; the action of the metal is almost wholly catalytic, although a certain amount undergoes oxidation. The peroxide oxidises mercury, its vapour blackening the metal, whilst the solution oxidises it to the black or yellow oxide or to white crystals. Platinum, zinc, aluminium, or magnesium in a finely-divided condition and red phosphorus are not oxidised by the peroxide; this substance slowly decolorises solutions of permanganic acid, but is without action on chromic, molybdic, or titanous acids. Hydrogen iodide and sulphide are both decomposed by the peroxide; sulphurous acid is converted into a mixture of sulphuric and ethyl sulphuric acids, whilst nitrous acid or ethyl nitrite yields ethyl nitrate. Amyl nitrite is resolved into ethyl nitrate and amyl alcohol.

The acyl chlorides and anhydrides, when treated with aqueous or alkaline solutions of the peroxide, yield the ethyl salts of the corresponding peracids. Acetic anhydride furnishes an oily product, probably ethyl peracetate, terephthalic chloride gives rise to *ethyl perterephthalate*, $C_6H_4(CO_3Et)_2$, a compound crystallising from benzene in plates melting

at 37° and exploding at higher temperatures or on percussion; the new substance behaves more like an anhydride than an ester, being hydrolysed by aqueous alkalis into ethyl hydroperoxide and terephthalic acid. Ethyl piperidine oxide (Wolfenstein, *Abstr.*, 1898, i, 536) is produced by the action of an aqueous solution of the peroxide on ethyl piperidine; primary and secondary bases are also attacked by the oxidising agent, but the products are indefinite.

Methyl hydroperoxide, an extremely explosive substance boiling at a lower temperature than its ethyl homologue, is produced, together with gaseous *dimethyl peroxide*, by the action of alkaline hydrogen peroxide solution on dimethyl sulphate. *Barium methyl hydroperoxide* crystallising in lustrous needles on adding alcohol to its concentrated aqueous solution, explodes when dry on trituration even at the ordinary temperature. G. T. M.

Nitrous Acid. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1901, 34, 755—762).—*Benzyl nitrite*, readily prepared by mixing together benzyl alcohol and sodium nitrite in a dilute sulphuric acid solution, is a pale yellow liquid boiling at 80—83° under 35 mm. pressure. It rapidly decomposes on keeping, with the formation of nitrous fumes and benzaldehyde. The compound described by Hollemann as benzyl nitrite boils 55° higher than the authors' compound (compare *Abstr.*, 1895, i, 455). Hydrogen peroxide, in dilute solutions, oxidises nitrous acid quantitatively to nitric acid, and decomposes the alkyl nitrites, yielding the corresponding alcohols and traces of their aldehydes. Ethyl hydroperoxide oxidises nitrous acid and ethyl nitrite to the corresponding nitrate; amyl nitrite, under these conditions, yielding amyl alcohol and an oil boiling at 85—90° and burning with a white flame. These reactions are readily explained on the assumption that the reagent acting on nitrous acid or its ester first forms an additive compound, in which the nitrogen atom is quinquivalent, the final product resulting from the elimination of water or an alcohol, and the formation of a derivative of tervalent nitrogen. G. T. M.

Addition of Hydrogen Fluoride to Salts of Ethyl Sulphuric Acid and certain Sulphonic Acids. By RUDOLPH F. WEINLAND and G. KAPPELLER (*Annalen*, 1901, 315, 357—378. Compare *Abstr.*, 1899, ii, 594).—The potassium and rubidium salts of certain organic derivatives of sulphuric acid combine with hydrogen fluoride when treated with aqueous solutions of this acid; this property, which is shared by some of the analogous caesium derivatives, is altogether wanting in the corresponding salts of sodium, ammonium, and the bivalent metals. The free sulphonic acids, excepting sulphanilic acid, which may be regarded as an internal salt, do not, under these conditions, combine with hydrogen fluoride. These additive compounds do not contain water of crystallisation.

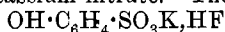
Potassium ethyl sulphate, when treated with 40 per cent. hydrofluoric acid, yields the additive compound, $\text{KEtSO}_4 \cdot \text{HF}$, crystallising in colourless needles; the corresponding rubidium salt is more soluble and requires for its formation 65 per cent. hydrofluoric acid; the caesium double salt could not be freed from the mother liquor.

Potassium ethanesulphonate and hydrofluoric acid yield an uncrys-

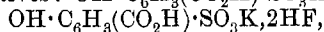
tallisable syrup, whilst taurine does not combine with hydrogen fluoride. The additive compounds of potassium methyl and propyl sulphates could not be isolated, and potassium phenyl sulphate is decomposed by hydrofluoric acid even at the ordinary temperature. The *double salts*, $C_6H_5 \cdot SO_3K, 2HF$ and $C_6H_5 \cdot SO_3Rb, 2HF$, produced by the action of 40—60 per cent. hydrofluoric acid on the corresponding benzene-sulphonates, crystallise in needles.

The compound $C_6H_4Me \cdot SO_3K, HF$, prepared from potassium *o*-toluenesulphonate, is fairly stable in air, and its crystallographic measurements show that it is not isomorphous with the hydrated salt $C_6H_4Me \cdot SO_3K, H_2O$, the former crystallising in the monoclinic system, the latter in the rhombic.

Potassium-*p*-toluenesulphonate yields two hydrogen fluoride compounds, $C_6H_4Me \cdot SO_3K, HF$ and $C_6H_4Me \cdot SO_3K, 2HF$, the former produced in a 40 per cent. solution of hydrofluoric acid, the latter obtained when the concentration is at least 65 per cent.; they both crystallise in prisms resembling potassium nitrate. The *double salts*,



and $OH \cdot C_6H_4 \cdot SO_3K, 2HF$, were obtained in a similar manner from potassium *p*-phenolsulphonate; only the *monohydrofluoride* could be isolated in the case of the rubidium salt; the corresponding caesium compound, $OH \cdot C_6H_4 \cdot SO_3Cs, HF$, crystallises in transparent, prismatic needles. Sulphosalicylic acid does not itself combine with hydrogen fluoride, but its potassium and rubidium salts yield with this reagent the following derivatives: $OH \cdot C_6H_3(CO_2H) \cdot SO_3K, HF$,



and $C_6H_3(OH)(CO_2H) \cdot SO_3Rb, HF$. The formation of the compound $NH_2 \cdot C_6H_4 \cdot SO_3H, 2HF$ from sulphanilic acid and 65 per cent. hydrofluoric acid is accompanied by a development of heat; the substance separates from the cooled solution in rhombic crystals which rapidly become turbid and decompose; it may also be produced by action of hydrogen fluoride on potassium sulphanilate. G. T. M.

Direct Nitration in the Aliphatic Series. By A. WAHL (*Compt. rend.*, 1901, 132, 693—695. Compare this vol., i, 4).—The compound $C_6H_9O_4N$, produced in small quantity by the action of a mixture of nitric and sulphuric acids on ethyl crotonate at temperatures below 25°, boils at 100—106° under 13 mm. pressure. The ester employed in this experiment was prepared by boiling for several hours a mixture of ethyl bromobutyrate and diethylaniline, the yield being 40—50 per cent. of the theoretical (compare Bischoff, *Abstr.*, 1899, i, 201). The ethyl salts of tiglic and *isolaunolic* acid do not yield nitro-derivatives on treatment with nitric acid, the latter ester giving rise to a nitrate, $C_{11}H_{18}O_2, HNO_3$, crystallising in colourless prisms and melting at 79°.

G. T. M.

Adamkiewicz's Proteid Reaction, Chemistry of Glyoxylic Acid. By F. GOWLAND HOPKINS and SIDNEY W. COLE (*Proc. Roy. Soc.*, 1901, 68, 21—33).—The proteid reaction described by Adamkiewicz (*Abstr.*, 1875, 172) is very uncertain; with some specimens of acetic acid little or no coloration is produced. The authors have found that the colour change which occurs is not due to furfuraldehyde, as

suggested by Udranszky (Abstr., 1888, 863), but to glyoxylic acid, small quantities of which are usually present in acetic acid. If a specimen of glacial acetic acid which yields the reaction is distilled, the glyoxylic acid collects in the earlier fractions, and the residue gives no coloration with proteid and sulphuric acid.

When acetic acid is heated with hydrogen peroxide in presence of ferrous iron, glyoxylic acid is produced, but is largely converted into formaldehyde. Glyoxylic acid is slowly formed when acetic acid is left exposed to the air and more rapidly in presence of ferrous iron and under the influence of direct sunlight.

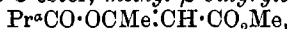
Glycol, glycollaldehyde, glycollic acid, oxalic acid, and pyruvic acid do not yield the Adamkiewicz reaction, which appears to be peculiar to glyoxylic acid. If the acetic acid is replaced by an aqueous solution of glyoxylic acid, the test becomes trustworthy; a solution suitable for the purpose is readily prepared by reducing a solution of oxalic acid with sodium amalgam. The proteid or proteid solution to be tested is first added to the reagent, and then strong sulphuric acid poured down the side of the test-tube; a brilliant violet-blue colour is produced at the junction of the liquids. E. G.

Synthesis and Properties of α -Dimethyl- β -ethylhydracrylic Acid. By B. SCHISCHKOWSKY and SERGIUS N. REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 158—163).—*aa-Dimethyl- β -ethylhydracrylic* [*β -hydroxy- $\alpha\alpha$ -dimethylvaleric*] acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CHEt}\cdot\text{OH}$, obtained by the action of zinc on a mixture of equivalent proportions of propaldehyde and ethyl α -bromoisobutyrate, crystallises from acetic acid in hexagonal plates and from water in large prisms melting at 103° . It has the normal molecular weight in freezing acetic acid and its mean electrical conductivity constant is $K\ 0\cdot00150$, the mean value for β -hydroxy-acids being $0\cdot00180$. The sodium, calcium, lead, silver, zinc, and barium salts were prepared. When distilled, the acid undergoes decomposition into propaldehyde and isobutyric acid, whilst under the action of hydriodic or sulphuric acid, it yields a lactone, $\text{C}_7\text{H}_{12}\text{O}_2$, melting at 52° , previously obtained by Anschütz and Gillet (Abstr., 1888, 1272). T. H. P.

Action of Butyryl Chloride on Methyl Sodioacetoacetate. By LOUIS BOUVEAULT and A. BONGERT (*Compt. rend.*, 1901, 132, 701—704. Compare Abstr., 1900, i, 474).—The action of acid chlorides on the sodium derivatives of the alkyl esters of acetoacetic acid results in the formation of two isomeric esters (compare Claisen, *Annalen*, 1897, 297, 2); the one corresponding with the ketonic form of the ester is indicated by the symbol C, and the other by the prefix O.

Methyl butyrylacetoacetate (C-ester), $\text{CPr}\cdot\text{O}\cdot\text{CHAc}\cdot\text{CO}_2\text{Me}$, produced by adding butyryl chloride to methyl sodioacetoacetate suspended in dry ether, is separated from the isomeric ester by means of a saturated solution of sodium carbonate in which the latter is insoluble; it is a colourless, slightly odorous liquid, boils at 105° under 14 mm. pressure, has a sp. gr. $1\cdot0978$ at 0° , and develops a coloration with ferric chloride. The copper derivative forms small blue crystals soluble in alcohol, chloroform, or ether, but insoluble in light petroleum; the sodium

derivative is a white, microcrystalline powder soluble in water and alcohol. The isomeric O-ester, *methyl β-butyryloxyacrylate*,



is a colourless liquid boiling at 104–105° under 10 mm. pressure; it yields no metallic derivatives and does not develop a coloration with ferric chloride.

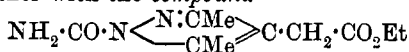
The O-ester is not attacked by water even in sealed tubes at 140–150°. The C-isomeride, on the other hand, is readily hydrolysed in boiling aqueous solutions into methyl alcohol, carbon dioxide, and butyrylacetone (Claissen and Ehrhardt, *Abstr.*, 1889, 850); it is also decomposed by the alkali hydroxides into acetic acid and *methyl butyrylacetate*; the latter compound, under these conditions, undergoes further hydrolysis, but is, however, obtained in a state of purity by the employment of ammonia and sodium methoxide as hydrolytic agents. Methyl butyrylacetate, a colourless liquid with a fruity odour, boils at 85° under 14 mm. pressure and has a density 1.037; its *copper* derivative melts at 128°.

Methyl β-butyryloxyacrylate is only slowly attacked by aqueous potassium hydroxide solution; the hydrolysis, however, proceeds more rapidly on heating, the products being methyl alcohol and potassium acetate and butyrate; when treated with an ethereal ammonia solution, the ester yields methyl acetoacetate and butyramide.

Methyl "dibutyrylacetate," $\text{COPr}^a\cdot\text{O}\cdot\text{CMe}\cdot\text{C}(\text{COPr}^a)\cdot\text{CO}_2\text{Me}$, is formed in small amount in the preceding condensation; it is a yellowish liquid and boils at 146° under 10 mm. pressure.

Methyl acetoacetate, when treated with ammonia gas, yields a trace of methyl β-aminocrotonate. G. T. M.

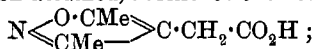
Ethyl Diacetylpropionate. By F. MARCH (*Compt. rend.*, 1901, 132, 697–699. Compare *Abstr.*, 1900, i, 374).—The *disemicarbazone*, $\text{CH}(\text{CMe}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, of ethyl ββ-diacetylpropionate is produced together with the *compound*



by the action of semicarbazide hydrochloride on the ester in the presence of sodium acetate; the two compounds are separated by extraction with ether, the latter dissolves and separates from the solvent in colourless crystals melting at 121–122°, whilst the former is very slightly soluble in the ordinary organic solvents and melts at 224–225°.

The *oxazole*, $\text{N}\begin{array}{c} \text{O}\cdot\text{CMe} \\ \diagup \quad \diagdown \\ \text{CMe} \end{array} \text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, obtained by heating on the water-bath a mixture of hydroxylamine hydrochloride, potassium carbonate, and ethyl ββ-diacetylpropionate, is an oil boiling at 152° under 25 mm. pressure; it is insoluble in water but miscible with ether or alcohol.

Alkaline hydrolysis of the preceding ester yields a solution of an alkali salt which, when acidified, furnishes the *acid*



this crystallises in needles melting at 122° and is readily dissolved in

water, alcohol, or ether. The *barium* salt, $\text{Ba}(\text{C}_7\text{H}_5\text{O}_3\text{N})_2 \cdot 2\text{H}_2\text{O}$, crystallises in needles soluble in water or alcohol and melts at $196-198^\circ$; the *cupric* and *silver* salts are obtained as green and white precipitates respectively, the *alkali* salts are very soluble and deliquescent. All attempts to obtain $\beta\beta$ -diacetylpropionic acid have proved of no avail, the ester on alkaline hydrolysis yielding a mixture of acetic and lævulic acids.

G. T. M.

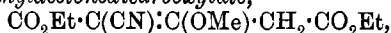
Osmyloxalates. By L. WINTREBERT (*Compt. rend.*, 1901, 132, 824—826. Compare Abstr., 1900, i, 543).—Sodium osmyloxalate, $\text{OsO}_2(\text{C}_2\text{O}_4)_2\text{Na}_2 \cdot 2\text{H}_2\text{O}$, may be produced by Vèzes' method from oxalic acid and an alkaline solution of osmium tetroxide, but is more easily prepared by treating the peroxide with a solution of oxalic acid and sodium hydrogen oxalate; the salt separates from concentrated solutions in reddish-brown crystals.

Ammonium osmyloxalate, $\text{OsO}_2(\text{C}_2\text{O}_4)_2(\text{NH}_4)_2 \cdot 2\text{H}_2\text{O}$, produced by heating at 80° for three weeks a concentrated solution of osmium tetroxide and ammonium hydrogen oxalate, separates in well-defined red crystals. In this preparation, the use of ammoniacal solutions must be avoided, since the ammonia reduces the peroxide, forming ammonium osmiamate, $\text{NH}_4\text{O} \cdot \text{OsO} \cdot \text{NO}$. The *silver* salt, $\text{OsO}_2(\text{C}_2\text{O}_4)_2\text{Ag}_2$, formed from silver nitrate and an alkali osmyloxalate, is employed in the preparation of the corresponding salts of the alkaline earth metals from their chlorides. The *barium* salt, $\text{OsO}_2(\text{C}_2\text{O}_4)_2\text{Ba} \cdot 4\text{H}_2\text{O}$, crystallises in greenish-yellow needles; the *strontium* and *calcium* salts are unstable, greenish-yellow powders, having a similar composition, the former crystallising with $4\text{H}_2\text{O}$ and the latter with $2\text{H}_2\text{O}$. An abnormal *barium* salt, $\text{OsO}_2(\text{C}_2\text{O}_4)_3\text{Ba}_2 \cdot 6\text{H}_2\text{O}$, produced by warming a solution of potassium or barium osmyloxalate, oxalic acid, and barium chloride, separates on cooling in yellowish-brown crystals.

G. T. M.

Properties of Acyl Derivatives of Ethyl Cyanoacetonedicarboxylate. Action of Cyanogen Chloride on Methyl Acetonedicarboxylate. By JUVÉNAL DERÔME (*Compt. rend.*, 1901, 132, 699—701. Compare Abstr., 1900, i, 426).—The compound $\text{NH}_2 \cdot \text{CO} \cdot \text{C}(\text{CN}) : \text{C}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ is obtained as a white, crystalline precipitate melting at 195° by the action of aqueous ammonia on ethyl cyanoethylacetonedicarboxylate. The formula given to this product corresponds with the enolic form of the parent ester; this view of its constitution is confirmed by the fact that the same substance is produced from the methyl and propyl derivatives of ethyl cyanoacetonedicarboxylate.

Ethyl cyanomethylacetonedicarboxylate,



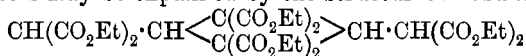
prepared by the action of methyl iodide on the silver derivative of ethyl cyanoacetonedicarboxylate suspended in ether, separates from this solvent in transparent crystals and melts at 70° ; it is slightly soluble in water but readily dissolves in chloroform.

Ethyl cyanopropylacetonedicarboxylate crystallises in colourless

needles and melts at 20° ; it resembles its lower analogue, and is prepared in a similar manner.

Methyl cyanoacetonedicarboxylate, $\text{CO}_2\text{Me}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, produced by the action of cyanogen chloride on the sodium derivative of methyl acetonedicarboxylate, melts at 64° ; its *copper* derivative is soluble in alcohol or chloroform, separates from solution in green crystals, and melts at 145° . G. T. M.

Bimolecular Ethyl Dicarboxyglutaconate. By MAX GUTHZEIT and A. WEISS (*Ber.*, 1901, **34**, 675—680. Compare Abstr., 1899, i, 115).—When a benzene solution of ethyl dicarboxyglutaconate (16 mols.) is left in contact with piperidine (1 mol.) at the ordinary temperature for some time, well developed rhombohedra of a *bimolecular ester*, $\text{C}_{30}\text{H}_{44}\text{O}_{16}$, melting at $102\text{--}103^{\circ}$, are deposited. When this is hydrolysed with dilute acids, a *bimolecular dicarboxyglutaconic acid* melting at 234° is obtained, but when hydrolysed with potassium hydroxide the ordinary unimolecular acid melting at 137° is formed. An isomeric bimolecular ester melting at $87\text{--}88^{\circ}$ is obtained when a 15 per cent. benzene solution of the ester melting at $102\text{--}103^{\circ}$ is left in contact with an excess of piperidine. Both esters are converted into the oily unimolecular esters when treated with sodium ethoxide and then with dilute acids, and both appear to be saturated compounds and do not give the ordinary enolic reactions. The isomerism for the two new esters may be explained by the structural formulæ



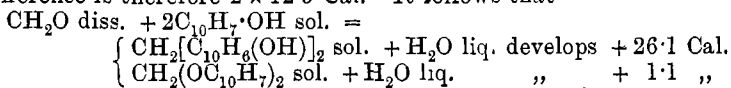
and $\text{C}(\text{CO}_2\text{Et})_2\cdot\text{CH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, but stereoisomerism is also possible.

The substance previously described as the ketonic form of ethyl isoacconitate is now shown to be a bimolecular ester, as on hydrolysis it yields von Pechmann's bimolecular glutaconic acid melting at 207° (Abstr., 1899, i, 870). J. J. S.

Velocities of Formation and Decomposition of Methylal at the Ordinary Temperature. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1901, [iii], **25**, 364—369).—The results of the author's experiments on the formation and decomposition of methylal (this vol., i, 254) are submitted to mathematical analysis, from which, however, no definite conclusions as to the mechanism of the reactions can be drawn, various different hypotheses being equally valid. N. L.

Heats of Formation of Acetals and their Isomerides. By MARCEL DELÉPINE (*Compt. rend.*, 1901, **132**, 777—779).—Comparison of the heats of formation of methylal and propylglycol, acetal and pinacone, glycol formal and propionic acid, glycol acetal and butyric acid, erythritol diformal and adipic acid, erythritol diacetal and suberic acid, mannitol triformal, and the homologue of tricarballic acid (calculated) shows that the difference between a formal and the isomeric acid varies from 2×21 Cal. to 4×18.9 Cal., and 6×17 Cal., seemingly becoming less as the number of $\cdot\text{O}\cdot$ linkings increases. With acetals, the values are somewhat lower, but are of the same order.

The heat of combustion of β -naphthol formal is 8335.6 cal., its molecular heat of combustion 2500.7 cal. at const. vol. and 2502.4 cal. at const. pressure, and its heat of formation 29.9 Cal., whilst the corresponding values for β -dinaphthylmethane, $\text{CH}_2[\text{C}_{10}\text{H}_6(\text{OH})]_2$, are 8252.2 cal., 2475.7 cal. and 2477.4 cal., and 54.9 Cal. The difference is therefore 2×12.5 Cal. It follows that



The formation of the formal is not reversible, but if the compound is heated at 100° with absolute alcohol containing a small quantity of hydrochloric acid it is converted into its isomeride. C. H. B.

Oxycelluloses. By A. NASTUKOFF (*Ber.*, 1901, 34, 719—723).—When either of the oxycelluloses formerly described (*Abstr.*, 1900, i, 540) is heated on the water-bath for 1—3 hours with 5 per cent. sulphuric acid, and after washing with water, with 10 per cent. aqueous sodium hydroxide for 10—30 minutes at 70 — 100° , it becomes easily soluble in water, especially at 100° ; heating with alkali alone is insufficient, and the sulphuric acid must be of greater concentration than 1 per cent. The oxycellulose prepared with permanganate requires to be heated for only 1 hour with the acid, but that obtained with bleaching powder requires $\frac{1}{3}$ hours. The 5—10 per cent. aqueous solutions obtained are as viscous as glycerol, and when evaporated on glass give lustrous, easily stripped, transparent films; they are not changed by keeping or boiling, yield precipitates with many mineral salts (for example, sodium chloride, barium chloride) and in this respect resemble Guignet's colloidal cellulose (*Abstr.*, 1889, 847). From this they differ, however, by reducing Fehling's solution and yielding yellow compounds with phenylhydrazine. On adding an acid to the aqueous solutions of the modified oxycelluloses, a precipitate is obtained which, if kept moist, can be redissolved, but if dried in the air, or washed with a weak acid, becomes insoluble; the solubility is restored, however, by heating with 10 per cent. aqueous sodium hydroxide. The phenylhydrazone prepared from the oxycellulose which has been rendered insoluble, is itself insoluble, but changes to the soluble form when heated with the alkali; the phenylhydrazone of the soluble oxycellulose, however, is directly soluble in water. As the soluble oxycelluloses contain a small quantity of combined alkali, they are probably the sodium salts of acids, which are themselves soluble in water but become converted into insoluble anhydrides or lactones on drying; the insoluble precipitates formed on adding iron, copper, and similar salts to the solutions of the oxycelluloses are probably insoluble salts of these acids. In empirical composition, the soluble oxycelluloses hardly differ from the original α -oxycellulose. They are not coloured by iodine, and do not give the phloroglucinol reaction in presence of hydrochloric acid.

β -Oxycellulose, obtained by the oxidation of cellulose with nitric acid, when heated with aqueous sodium hydroxide alone without preliminary treatment with sulphuric acid, becomes soluble in water, but the solutions obtained, although similar to those from α -oxycel-

lulose, dry on to glass in the form of a hard, firmly-adhering film which, when removed, breaks up into a dull powder. The new, soluble substances are therefore not identical with β -oxycellulose, and to distinguish them they are provisionally termed γ -oxycelluloses.

W. A. D.

Formation of Secondary *s*-Acid Hydrazides. By ROBERT STOLLÉ (*Ber.*, 1901, **34**, 681—682. Compare Abstr., 1899, i, 413, and Autenrieth and Spiess, this vol., i, 230).—A very good method for the preparation of secondary *s*-acid hydrazides is to heat the primary hydrazides with acid anhydrides to a fairly high temperature.

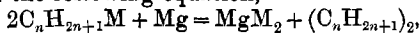
s-Dibutrylhydrazide melts at 167°, not at 162—163°, distils at 214° under 24 mm. pressure, and is insoluble in dry ether. Dibenzoylhydrazide melts at 238°, and not at 233°.

J. J. S.

Action of Acid Chlorides and Anhydrides on the Organometallic Compounds of Magnesium. By TISSIER and VICTOR GRIGNARD (*Compt. rend.*, 1901, **132**, 683—685. Compare this vol., i, 250).—The acid chlorides and anhydrides of the organic acids react very violently with the magnesium alkyl iodides, and in practice the reagents are diluted with ether and cooled with ice. The action takes place in two stages, the addition of 1 mol. of magnesium methyl iodide to acetyl chloride giving rise to the substance $\text{CMe}_2\text{Cl} \cdot \text{OMgI}$, whilst a second mol. of the organometallic iodide furnishes the final product $\text{CMe}_3 \cdot \text{OMgI}$, this compound, on treatment with water, yielding trimethylcarbinol. When acetic anhydride is employed, the intermediate product has the composition $\text{OAc} \cdot \text{CMe}_2 \cdot \text{OMgI}$, the final result being the same as in the preceding example. When benzoyl chloride or oxide is substituted for its acetic analogue, a similar series of reactions gives rise to phenyldimethylcarbinol; this compound, formerly described as a liquid, is, in reality, a solid melting at 23° and boiling at 89—90° under 10 mm. pressure (compare Abstr., 1900, i, 382). The alcohol, when distilled under the ordinary pressure, decomposes into water and β -phenylpropylene, $\text{CMePh} \cdot \text{CH}_2$, an olefine boiling at 158—160° under 8 mm. pressure.

G. T. M.

Organometallic Compounds of Magnesium. By TISSIER and VICTOR GRIGNARD (*Compt. rend.*, 1901, **132**, 835—837. Compare Abstr., 1900, i, 382).—The saturated hydrocarbons may be prepared in a state of purity by dropping a mixture of ether and water on to the magnesium alkyl haloids maintained at 0°. When an alkyl haloid is added to magnesium, two reactions occur, one involving the formation of the corresponding magnesium alkyl haloid, and the second, which gives rise to a higher hydrocarbon, taking place in accordance with the following equation,



where M is the halogen radicle. The second reaction, which takes place only to a limited extent among the lower members of the series, becomes more pronounced as the alkyl radicle involved increases in complexity. At the C_6 term both actions take place to the same extent. Magnesium decomposes ethylene dibromide, causing the evolution of ethylene; a similar reaction takes place with other haloid

compounds containing 2 atoms of the halogen. When an alcohol is added to a magnesium alkyl haloid, the following reaction occurs, $C_nH_{2n+1}MgM + R^I R^{II} R^{III} C \cdot OH = C_nH_{2n+2} + R^I R^{II} R^{III} CO \cdot MgM$. The new organometallic derivatives are obtained crystalline; they are decomposed by water, regenerating the alcohol. Phenol and methyl, ethyl, and amyl alcohols react in this manner with magnesium ethiodide.

Magnesium readily dissolves in methyl alcohol, forming magnesium methoxide, $Mg(OMe)_2$, a white substance readily decomposed by water; the metal is not very soluble in ethyl alcohol, even at its boiling point, the ethoxide being formed, however, when the reaction is carried out in sealed tubes.

G. T. M.

Action of the Esters of Dibasic Acids on Organometallic Compounds. By AMAND VALEUR (*Compt. rend.*, 1901, 132, 833—834. Compare this vol., i, 246, 249).—The author has applied the Wagner-Saytzeff reaction to esters of the oxalic acid series. The pinacone of acetone results from the interaction of magnesium methiodide and ethyl oxalate. Ethyl malonate, when treated with magnesium ethiodide, yields an unsaturated alcohol, $C_{11}H_{22}O$, boiling at 177—178°; this compound is probably formed by the dehydration of the glycol, $OH \cdot CEt_2 \cdot CH_2 \cdot CEt_2 \cdot OH$.

The glycol, $OH \cdot CEt_2 \cdot CH_2 \cdot CH_2 \cdot CEt_2 \cdot OH$, prepared from ethyl succinate and magnesium ethiodide, crystallises from benzene and melts at 70°.

G. T. M.

New Reactions of Organometallic Compounds of Magnesium. By CHARLES MOUREU (*Compt. rend.*, 1901, 132, 837—839. Compare preceding abstracts).—Amyl nitrite and nitroethane, when treated with magnesium ethiodide, yield products which, on treatment with water, give rise to diethylhydroxylamine. Methyl nitrate interacts violently with magnesium methiodide, the product, when treated with water, yielding a basic substance boiling at 95°, and having the properties of a hydroxylamine derivative, probably dimethylhydroxylamine.

G. T. M.

Ethereal Derivatives of the Organometallic Compounds. By EDMOND E. BLAISE (*Compt. rend.*, 1901, 132, 839—841. Compare Grignard, *Abstr.*, 1900, i, 382).—When an alkyl haloid reacts with magnesium in the presence of dry ether, a substance is formed containing the elements of the solvent, the compounds, $Et \cdot MgI, Et_2O$ and $Et \cdot MgBr, Et_2O$, being obtained from ethyl iodide and ethyl bromide respectively. The latter of these substances is remarkably stable, and does not lose its ether even at 145°.

These compounds form crystalline derivatives with certain nitriles, the products still containing the elements of ether; the following substances of this type have been prepared: $CEtPh \cdot N \cdot MgI, Et_2O$, $CEtPh \cdot N \cdot MgBr, Et_2O$, and $C_6H_4Me \cdot CEt \cdot N \cdot MgI, Et_2O$.

Ether plays an essential part in the formation of organometallic magnesium compounds, and the reaction between the metal and the alkyl iodide does not take place when this solvent is replaced by some other medium.

G. T. M.

The Benzene Ring System. By HUGO KAUFFMANN (*Ber.*, 1901, 34, 682—698. Compare Abstr., 1900, i, 480).—It is shown by reference to numerous specific examples that those benzene compounds which, in the form of vapour, are capable of absorbing Tesla rays and transforming them into violet light are also the compounds which have been shown by Perkin (*Trans.*, 1896, 69, 1025) to possess abnormal molecular magnetic rotation.

The magnetic rotations of all such substances are much higher (in some cases even 100 per cent.) than those calculated from the sum of the atomic rotations, and it is exactly those compounds which give highly luminous vapours which possess the greatest abnormality. The same compounds also appear to have abnormally high molecular refraction, and still higher molecular dispersion, coefficients.

J. J. S.

Electrolytic Oxidation of Toluene. By KARL PULS (*Chem. Zeit.*, 1901, 25, 263).—The experiments were similar to those of Merzbacher and E. F. Smith (this vol., i, 134), and gave similar results. Benzaldehyde, ethyl benzoate, and *p*-sulphobenzoic acid were obtained; of benzoic acid itself, but a small quantity was detected. No formation of phenose, $C_6H_6(OH)_6$ (Rénard, Abstr., 1881, 721), could be observed.

C. F. B.

Simultaneous Formation of Isomeric Substitution Derivatives of Benzene. By ARNOLD F. HOLLEMANN (*Rec. Trav. Chim.*, 1900, 19, 364—376).—The author has studied the composition of the product of the nitration of bromobenzene by the method of solidifying points, as in the case of the nitration of chlorobenzene (Abstr., 1900, i, 638), and by the method of sp. gr. as in the case of the nitration of nitrobenzene (Abstr., 1900, i, 387). In order to prevent the formation of bromodinitrobenzene, the nitric acid used must contain 4 parts of acid of sp. gr. 1.48 to 1 part of acid of sp. gr. 1.52, and the temperature be kept at 0° or at -30° by solid carbon dioxide and alcohol. The method of solidifying points gave, for the composition of the product obtained at 0°, 38.3 per cent. of ortho-, and 61.7 per cent. of para-bromonitrobenzene; the method of sp. gr. gave at the same temperature 0.3 per cent. of the meta-, 37.2 per cent. of ortho-, and 62.5 per cent. of para-compound. For the product obtained at -30°, the second method gave 0.3 per cent. of meta-, 34.4 per cent. of ortho-, and 65.3 per cent. of para-bromonitrobenzene.

On comparing these values with those previously obtained (*loc. cit.*), it is seen that the proportion of *o*-nitro-derivative formed is greater with bromobenzene than with chlorobenzene, and that the ratio of the amounts of ortho- and para-compound formed is independent of the temperature. Thus, with similar compounds, such as chloro- and bromo-benzene, the velocity constants of their action with nitric acid is affected by temperature in the same degree. It is noteworthy that the ratio of the quantities of *o*-chloro- and *o*-bromo-benzene corresponding with 100 parts of *p*-chloro- and *p*-bromo-benzene (0.694) is nearly the same as the ratio of the mol. wts. of chloro- and bromo-benzene (0.716).

W. A. D.

Action of Silver Nitrite on Aromatic Halogen-substituted Compounds. By B. ZNATOWICZ (*Bull. Acad. Sci. Cracow*, 1900, 399—400).—The author shows that (1) by the action of silver nitrite on aromatic substances containing halogen in the benzene nucleus, the nitro-group replaces the halogen; (2) iodine is most readily replaced, chlorine least readily; (3) the presence of other groups increases the ease with which the reaction with silver nitrite takes place; (4) oxidation is effected by the silver nitrite at temperatures at which it decomposes.

K. J. P. O.

Tervalent Carbon. A Reply. By MAX GOMBERG (*Amer. Chem. J.*, 1901, 25, 317—335. Compare Norris, this vol., i, 198).—According to the author, hydrogen is not evolved when zinc acts on triphenylchloromethane in perfectly dry ethyl acetate or ether. The unsaturated hydrocarbon is formed in the absence of air, and may be obtained in a practically pure form as large, pale-yellow crystals, but if air is admitted the insoluble peroxide is deposited. The evolution of hydrogen observed by Norris is due to the presence of alcohol and water in his ethyl acetate, as when these compounds are present part of the triphenylchloromethane is hydrolysed or etherified and the hydrogen chloride thus produced acts on the zinc. The yield of peroxide is always much less when moist solvents are employed.

Solutions of hydrogen chloride in dry benzene in contact with zinc evolve hydrogen, although the electrical conductivities of such solutions are practically *nil*.

The fact that the addition of benzene to a mixture of ether and sodium retards the evolution of hydrogen is due, according to the author, to the formation of a slimy protective layer round the sodium.

Various experiments are described which go to prove that (a) metals do not cause the evolution of hydrogen chloride from triphenylchloromethane; (b) dry air converts the unsaturated hydrocarbon into its peroxide (compare Norris, *loc. cit.*); (c) the unsaturated compound is probably colourless.

J. J. S.

Phosphates of Aromatic Amines and the Dependence of their Formation and Stability on their Composition and Structure. By P. N. RAIKOW and P. SCHATBANOW (*Chem. Zeit.*, 1901, 25, 219—222, 243—245, 261—262, 279—281).—In order to elucidate the influence of the nature and position of substituting groups, the reaction of a number of aromatic amines with phosphoric acid was studied, the amine being warmed with acid of sp. gr. 1.7; the stability of the phosphate formed was also investigated, the salt being subjected to treatment with water, alcohol, and ether. The following regularities were observed: (1) In the presence of foreign solvents (water, alcohol, ether) none of the aromatic bases examined forms a triphosphate. (2) Only aniline and benzylamine form triphosphates when the base is present in excess. (3) When the acid is present in excess, all bases that react with phosphoric acid at all form monophosphates, except *m*- and *p*-aminobenzenesulphonic acids, which form triphosphates; they are the only derivatives of aniline that form triphosphates. (4) With these two exceptions, the derivatives of aniline do not form triphosphates, even when excess of the base is

present, but only di- or mono-phosphates or none at all. (5) The substitution of any group in aniline lowers the power of combining with phosphoric acid and the stability of the compound formed. (6) The chemical nature of the substituting group exerts an influence. (7) So does its combining weight, the group of greater weight often exerting the greater influence. (8) So does its position, the influence being greatest in the ortho-, least in the para-position. (9) Water, alcohol, and ether eliminate the base from these phosphates, either wholly, or partially with formation of more acid phosphates. *m*-Phenylenediamine diphosphate, however, is not altered by boiling with water, and β -naphthylamine monophosphate is converted into a diphosphate. (10) Bases with nitrogen in a ring, such as pyrroline, piperidine, quinoline, and *iso*quinoline, only form monophosphates. (11) A benzene ring in the ortho-position exerts the same influence as other substituents; in the meta- and para-positions, on the other hand, it increases the power of combination with phosphoric acid, and this indifferently whether it is attached directly to the main ring as in β -naphthylamine, or quite indirectly as in benzidine and aminoazobenzene.

The phosphates of the aromatic amines are very stable in air and light; apparently they are the form in which the amines are best preserved permanently. The differences which the amines exhibit in their power of combining with phosphoric acid may be utilised in order to separate them in many cases. The phosphates prepared, not always for the first time, are those of the following bases. *Aniline*, *mono*-, *di*- (the most stable; melts at 180°), and *tri*-phosphates. *o*-, *m*-, and *p*-*Toluidines*, each *mono* and *di*. 1:3:5-*Xylidine*, *mono* and *di*; 1:3:6, *mono* only. ψ -*Cumidine*, *mono*. *Chloroanilines*, *o*- and *m*-, *mono* and *di*; *p*, *mono* (if no *di*, only because the amine is solid and the excess of it could not be separated from the salt). *Bromoanilines*, *o*, *mono* only; *m*, *mono* and *di*; *p*, *mono*. *Di*- and *tri*-*bromoaniline*, none. 3:5-*Dibromo*-2:4-*xylidine*, *mono*. *p*-*Iodoaniline*, *mono*. *o*- and *p*-*Hydroxyaniline*, *mono* (a crystalline meta-salt could not be obtained). *o*-*Aminothiophenol*, *mono*. *o*-*Anisidine*, *mono*. *p*-*Phenetidine*, *mono* and *di*. *Nitroanilines*, *o*, none; *m* and *p*, *mono*. *Nitrotoluidines*, $\text{NH}_2 : \text{NO}_2 : \text{CH}_3 = 1:2:4$, $1:3:4$, $1:3:6$, and $1:2:4$, *mono*. *Picramic acid* and *trinitroaniline*, none. *Aminobenzoic acids*, *o*, *m*, and *p*, *mono*. *Aminobenzenesulphonic acids*, *m* and *p*, *tri*. *m*-Phenylenediamine phosphate, $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot 2\text{H}_3\text{PO}_4$. *p*-Phenylenediamine and *diaminotetrahydroxybenzene*, none. *Benzylamine*, *mono*, *di*, and *tri*. *Phenylhydrazine*, *mono* and *di*. *Tolylhydrazines*, *o*- and *p*-, *mono*. *Acetyl*- and *benzoyl*-phenylhydrazine, none. *Aminoazobenzene*, *mono*. *Pyrrole*, *mono*. *Piperidine*, *mono*. Benzidine phosphates, $\text{C}_{12}\text{H}_8(\text{NH}_2)_2 \cdot 2\text{H}_3\text{PO}_4$ and $\text{C}_{12}\text{H}_8(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$.

Naphthylamines, α , *mono*; β , *mono* and *di*. *Quinoline*, *mono*. *iso*Quinoline, *mono*.
C. F. B.

New Synthesis of Aniline. By GEORGE F. JAUBERT (*Compt. rend.*, 1901, 132, 841—842).—Aniline or *p*-toluidine may be synthesised from benzene or toluene, and obtained in the form of hydrochloride by heating together hydroxylamine hydrochloride and the corresponding

hydrocarbon in the presence of aluminium or zinc chloride; the yield obtained by this method is not, however, very good. G. T. M.

Halogen-substituted Aminomercaptans. By ALEXANDER EIBNER (*Ber.*, 1901, **34**, 657—660).—When trichloroethylidenedianiline, $\text{CCl}_3\cdot\text{CH}(\text{NPh})_2$, is mixed with thioacetic acid, hydrogen sulphide is evolved, and acetanilide and *acetylphenyl- α -aminotrichloroethylhydrosulphide*, $\text{CCl}_3\cdot\text{CH}(\text{SH})\cdot\text{NAcPh}$, are obtained. The latter substance melts at 99° ; it appears to be the first instance met with of an α -aminohydrosulphide, that is one in which the amino-group and sulphur atom are attached to the same carbon atom; it is not a very stable substance; dilute acids readily decompose it into chloral, hydrogen sulphide, and acetanilide.

When benzylidenedianiline, $\text{NPh}\cdot\text{CHPh}$, is dissolved in a mixture of light petroleum and ether, and thioacetic acid is added, a substance, $\text{NAcPh}\cdot\text{CHPh}\cdot\text{SH}$, melting at 75° , is obtained; this is unstable, decomposing readily into acetanilide and thiobenzaldehyde.

Thioacetic acid does not react readily with phenylthiocarbimide; at 200° , acetanilide and carbon disulphide are, however, formed. Addition probably takes place as an intermediate stage. C. F. B.

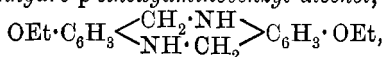
Nitro-derivatives of *o*-Anisidine. By GEORGES FREYSS (*Bull. Soc. Ind. Mulh.*, 1900, **70**, 375—383).—By the action of nitric acid on acetyl-*o*-anisidine, two mononitro-derivatives are produced. *p*-Nitro-*o*-acetylanisidine, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NH}_2$, $[\text{OMe}:\text{NH}_2:\text{NO}_2 = 1:2:5]$, melts at 153 — 154° , and is hydrolysed to *p*-nitro-*o*-anisidine melting at 139 — 140° ; by replacing the amino-group with hydrogen, the latter compound is converted into *m*-nitroanisole; the constitution of the nitroanisidine was established by reducing it to the *p*-diamine melting at 220° , and by converting it by means of alkali hydroxide into *p*-nitroguaiacol, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{OH}$ $[\text{OMe}:\text{OH}:\text{NO}_2 = 1:2:5]$. The *ethyl* ether of *p*-nitroguaiacol melts at 85 — 86° , and is converted by reduction and acetylation into a *methoxyphenacetin*, $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NHAc}$, $[\text{OMe}:\text{OEt}:\text{NHAc} = 1:2:5]$.

m-Nitro-*o*-anisidine, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{OMe}$ $[\text{OMe}:\text{NH}_2:\text{NO}_2 = 1:2:4]$, melts at 116.5 — 117.5° , is identical with the nitroanisidine produced by the reduction of dinitroanisole (Cahours, *Annalen*, 1850, **74**, 301), and is converted by elimination of the amino-group into *p*-nitroanisole, thus establishing its constitution. The *acetyl* derivative melts at 175 — 176° ; it is produced by the action of nitric acid on acetyl-*o*-anisidine, and is the sole product of the action when the nitration is carried out in sulphuric acid solution with 1 mol. of nitric acid.

The two nitroacetylanisidines described above are converted by further nitration into Meldola and Wechsler's dinitroacetanilide (*Trans.*, 1900, **77**, 1172), thus establishing the position of the nitro-groups in the latter. Attempts to eliminate the amino-group from dinitro-*o*-anisidine gave the monomethyl ether of *o*-nitroresorcinol $[\text{OMe}:\text{OH}:\text{NO}_2 = 1:3:4]$, one of the nitro-groups being replaced by hydroxyl; the *dimethyl* ether, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{NO}_2$, $[(\text{OMe})_2:\text{NO}_2 = 1:3:4]$, melts at 72 — 73° , and is reduced to aminodimethylresorcinol (Bechhold, *Abstr.*, 1889, 1155).

T. M. L.

Action of Formaldehyde on *p*-Formylphenetidine. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1901, 25, 178. Compare Abstr., 1900, i, 285, 436).—*p*-Formylphenetidine is decomposed by strong hydrochloric acid in the cold. It dissolves in excess of formaldehyde; from the solution, water precipitates an oil which decomposes spontaneously into formaldehyde and *p*-formylphenetidine. If the solution is allowed to remain in the cold with a very little dilute hydrochloric acid, however, crystalline *anhydro-p-ethoxyaminobenzyl alcohol*,



melting at 140°, is formed.

Valerylamine and valeryl-*p*-phenetidine yield amorphous *p*-anhydrovalerylaminobenzyl and anhydrovalerylethoxyaminobenzyl alcohols respectively when heated with excess of formaldehyde and strong hydrochloric acid. C. F. B.

Reactions of Nitroxyl [NOH]. By ANGELO ANGELI and FRANCESCO ANGELICO (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 164—168. Compare Abstr., 1900, ii, 594).—Salts of nitrohydroxylaminic acid are readily resolved into the corresponding nitrites and the unsaturated residue nitroxyl, :N·OH, which, in presence of aldehydes, nitroso-derivatives, amines, &c., yields additive products. This reaction has been further studied, the results being as follows.

Benzaldehyde, anisaldehyde, piperonylaldehyde, acetaldehyde, and formaldehyde react with salts of nitrohydroxylaminic acid, yielding the corresponding substituted hydroxamic acids.

With nitrosobenzene and nitroso-*p*-toluene, salts of nitrohydroxylaminic acid give the nitroso-derivatives of phenylhydroxylamine and *p*-tolylhydroxylamine respectively.

The additive compounds formed by the action of nitrohydroxylaminates with aliphatic secondary amines (piperidine and coniine) give up water, the residues of 2 mols. then uniting to form tetrazones.

T. H. P.

Iodo-derivatives of Phenol. By P. BRENANS (*Compt. rend.*, 1901, 132, 831—833).—A mixture of 2:4-diiodophenol and 2:4:6-triiodophenol is obtained on adding a potassium hydroxide solution of phenol, containing excess of the alkali, to a potassium iodide solution of iodine; the quantities of these derivatives produced depend on the relative proportions of phenol and iodine employed in the experiment; when the latter substance is in considerable excess and the solution is rendered strongly alkaline, diiodophenol iodide is precipitated as a violet-red, amorphous compound. The acetyl derivative of 2:4-diiodophenol melts at 70—71°, not at 76° as stated by Neuman and Vater (*Annalen*, 1887, 241, 81). G. T. M.

The Supposed Dinaphthylene Alcohol. By R. FOSSE (*Compt. rend.*, 1901, 132, 695—697. Compare Rousseau, Abstr., 1882, 735, 1211, 1299).—On applying Tiemann and Riemer's reaction to β -naphthol, Rousseau obtained, together with other products, a substance which decomposed at 260°, and was supposed by him to be dinaphthylene alcohol, C₂₂H₁₄O. The author shows that this compound has, in reality,

the empirical formula $C_{31}H_{20}O_2$, and is the *esoanhydride* of 2 : 2' : 2''-tri-hydroxy-1 : 1' : 1''-trinaphthylmethane, $OH \cdot C_{10}H_6 \cdot CH < \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} > O$; it is produced by the action of chloroform on sodium β -naphthoxide in sealed tubes at 150° , and may also be prepared synthetically from 2-hydroxy-1-naphthaldehyde and β -naphthol by condensation in acetic acid solution in the presence of sulphuric acid. The compound is obtained pure by repeated crystallisation, first from nitrobenzene, and then from acetone; when separating from the latter medium, the crystals contain a certain amount of the solvent, and when freed from this, melt at 273° to a brown liquid; it is insoluble in aqueous alkalis, but dissolves in their alcoholic solutions. The *acetyl* derivative of the preceding compound melts at 285° .
G. T. M.

Naphthylol-naphthyl-oxynaphthylmethane. By R. FOSSE (*Compt. rend.*, 1901, 132, 787—789).—A more detailed account of *naphthylol-naphthyl-oxynaphthylmethane* [*esoanhydride* of 2 : 2' : 2''-tri-hydroxy-1 : 1' : 1''-trinaphthylmethane] (preceding abstract). Its *methyl* ether melts at 255° , and its *ethyl* ether at 304° . Cryometric determinations with the former show that its molecular weight is 438.

C. H. B.

Acidimetric Value of Monosubstituted Benzoic Acids. By GUSTAVE MASSOL (*Compt. rend.*, 1901, 132, 780—781).—The author has determined the heat of formation, from solid acid and solid alkali hydroxide, of the solid anhydrous salts of the monosubstituted derivatives of benzoic acid.

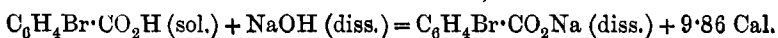
| | Ortho. | Meta. | Para. |
|----------------------------|-------------|-------------|-------------|
| Sodium hydroxybenzoate ... | +19.15 Cal. | +17.77 Cal. | +17.79 Cal. |
| „ bromobenzoate | +17.99 „ | | +17.39 „ |
| „ chlorobenzoate | +18.87 „ | | |
| „ iodobenzoate | +17.73 „ | | |
| „ nitrobenzoate | +20.36 „ | +19.39 „ | +19.31 „ |

The heat of formation of sodium benzoate is +17.40 Cal., and the somewhat varying effect of the substitutions is readily recognised. In the ortho-derivatives, the nitro-group has the greatest effect, and the hydroxyl group comes next. In the meta- and para-derivatives the nitro-group has a relatively large effect, whilst the hydroxyl group has very little effect.

C. H. B.

Thermochemistry of *o*-Chloro- and *o*-Iodo-benzoic Acids. By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1901, [iii], 25, 195—196. See this vol., ii, 226).

Thermochemistry of *o*- and *p*-Bromobenzoic Acids. By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1901, [iii], 25, 369—371).—The solubility of *o*-bromobenzoic acid in water is too small to allow of its heat of dissolution being determined. The sodium salt becomes anhydrous at 110° , and dissolves in water with the development of 3.08 Cal. From the heat of neutralisation,



the heat of formation of the anhydrous sodium salt from the solid base and acid is calculated to be 17.99 Cal.

The heat of dissolution of *p*-bromobenzoic acid also could not be determined. The sodium salt becomes anhydrous at 100°; its heat of dissolution is -0.38 Cal. From the heat of neutralisation,

$C_6H_4Br \cdot CO_2H$ (sol.) + NaOH (diss.) = $C_6H_4Br \cdot CO_2Na$ (diss.) + 5.80 Cal., the heat of formation of the anhydrous salt is calculated to be 17.39 Cal., all the substances concerned being in the solid state. This result is almost identical with the corresponding value (17.4 Cal.) for sodium benzoate. The progressively decreasing influence of substituted chlorine, bromine, and iodine is well shown in the heats of formation of sodium benzoate (17.4 Cal.), *o*-chlorobenzoate (18.87 Cal.), *o*-bromobenzoate (17.99 Cal.), and *o*-iodobenzoate (17.73 Cal.).

N. L.

Conversion of Anethole into Anisic Acid by Five successive Oxidations. By J. BOUGAULT (*Compt. rend.*, 1901, 132, 782—784).—Methoxyhydratropic acid, obtained (Abstr., 1900, i, 495) by the action of silver oxide on the aldehyde prepared by oxidising anethole with mercuric oxide and iodine, is in its turn oxidised by chromic mixture and converted into *p*-methoxyacetophenone. This ketone, when oxidised by potassium permanganate in alkaline solution, yields *p*-methoxyphenylglyoxylic acid. This is converted into anisic acid by the action of permanganate in acid solution. C. H. B.

Metallic "Saccharinates." By H. DEFOURNEL (*Bull. Soc. Chim.*, 1901, [iii], 25, 322—329).—Only the sodium, potassium, barium, and silver derivatives of "saccharin" (*o*-benzoisulphinide) seem to have hitherto been described. The *lithium, copper, calcium, strontium, magnesium, zinc, mercury, cadmium, lead, manganese, cobalt, iron, and nickel* salts have therefore been prepared and analysed, and are described in the paper; they are obtained either by the action of "saccharin" on the metallic carbonates or by double decomposition from the sodium derivative and the metallic sulphates. N. L.

A Simple Synthesis of δ -Ketonic Acids. By HANS STOBBE [and in part HANS VOLLAND] (*Ber.*, 1901, 34, 653—656).—When a mixture of acetophenone and ethyl cinnamate is added gradually to a suspension of sodium ethoxide in ether, cooled in a freezing mixture, and the whole is allowed to remain at first in the freezing mixture, afterwards at the ordinary temperature, partial condensation takes place with formation of γ -benzoyl- β -phenylbutyric acid,



(Vorländer and Knöttsch, Abstr., 1897, 286); this can be separated from uncondensed cinnamic acid by means of its *semicarbazone*, which is but little soluble in dilute alcohol, and melts at 212.5—213°.

C. F. B.

New Derivatives of Dimethylaminobenzoylbenzoic Acid. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1901, 132, 746—750. Compare Abstr., 1900, i, 170; this vol., i, 146, 276).—*Nitrodimethylaminobenzoylbenzoic acid* forms small, yellow prisms containing $1H_2O$, which is lost at about 100°, the anhydrous acid

melting at 170° . When heated with sulphuric acid and mercuric sulphate, it yields phthalic acid. Methyl dimethylaminobenzoylbenzoic acid forms yellow prisms insoluble in water and only slightly soluble in cold organic solvents, but soluble in the latter on heating. It melts at 140° , and not 163° as stated by Limpricht (*Annalen*, 1899, 307, 307), whose product was probably *p*-nitrodimethylaniline *Nitrodimethylanilinephthalein*, obtained by the condensation of dimethylaniline with nitrodimethylaminobenzoylbenzoic acid in presence of acetic acid, crystallises from a mixture of alcohol and chloroform in orange prisms melting at 175° ; it forms salts which are readily decomposed by water. When reduced, it yields *aminodimethylanilinephthalein* in white needles melting at 179° ; its *acetyl* derivative forms colourless prisms which melt at 157° . An isomeride of the latter, crystallising in colourless prisms which melt at 209° and are much more soluble in alcohol, is obtained by condensing dimethylaminobenzoylbenzoic acid with *m*-aminodimethylaniline in presence of acetic anhydride.

In the nitrodimethylaminobenzoylbenzoic acid, the nitro-group is most probably in the ortho-position with respect to the dimethylamino-group.
C. H. B.

*iso*Alantolactone, a Bye-product in the Preparation of Alantolactone. By JULIUS SPRINZ (*Ber.*, 1901, 34, 775—781).—*iso*Alantolactone, described by Dumas (*Arch. de Pharm.*, 1835, 15, 158) as 'helenin,' and regarded by Kallen as having the composition $(C_6H_5O)_n$ (*Abstr.*, 1874, 352) melts at 115° , has the empirical formula $C_{15}H_{20}O_2$, and a corresponding molecular weight, as determined from the freezing point of a solution in benzene. By warming with sodium hydroxide, it is hydrolysed to *iso*alantolic acid, $OH \cdot C_{14}H_{20} \cdot CO_2H$, of which the *silver*, *barium*, and *calcium* salts are also described. The *ethyl* ester separates from absolute alcohol in colourless, rhombic crystals. The *amide* crystallises from alcohol in white needles and melts at 237 — 239° ; its *acetyl* derivative, $C_{17}H_{25}O_3N$, crystallises from acetic acid and melts at 212° .

Dihydroisoalantolactone, $C_{15}H_{22}O_2$, prepared by the action of sodium amalgam on the lactone, melts at 166° . The *acid*, $C_{15}H_{24}O_3$, melts at 122 — 123° . The *amide*, $C_{15}H_{25}O_2N$, forms prismatic needles and melts at 176° .

*iso*Alantolactone *monohydrochloride*, $C_{15}H_{20}O_2 \cdot HCl$, crystallises from hot alcohol in colourless needles and melts at 153° . The *dihydrochloride*, $C_{15}H_{20}O_2 \cdot 2HCl$, was obtained as a syrupy liquid.

*iso*Alantolactone yields a nitro-derivative, and when distilled with zinc dust appears to give traces of naphthalene; it has not been converted into alantolactone.
T. M. L.

Esterification of 3-Nitrophthalic Acid. By RUDOLF WEGSCHEIDER (*Ber.*, 1901, 34, 680—681. Compare this vol., i, 32).—In reply to Marckwald and McKenzie (this vol., ii, 229), the author points out that he had previously observed the formation of normal ester but not of the isomeric acid ester as the amount of acid employed was small.

J. J. S.

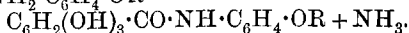
Peracids and Peroxide Acids derived from Dibasic Organic Acids. By ADOLF BAEYER and VICTOR VILLIGER (*Ber.*, 1901, 34, 762—767. Compare Pechmann and Vanino, *Abstr.*, 1894, i, 416. Thiele, *Abstr.*, 1896, i, 597).—*Monoperphthalic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_3\text{H}$, prepared by shaking together finely divided phthalic anhydride and an alkaline solution of hydrogen peroxide until the former passes into solution, is extracted by ether from the acidified solution and crystallises from this solvent in needles decomposing at 110° . The compound resembles perbenzoic acid, liberating iodine from hydriodic acid and oxidising aniline to nitrosobenzene; it may also be obtained by hydrolysing phthalic peroxide with cold sodium hydroxide solution.

Phthalic acid peroxide, $\text{O}_2(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$, is produced either by treating the alkaline solution of the preceding compound with phthalic anhydride or by the direct action of hydrogen peroxide solution on finely divided phthalic anhydride in the presence of sodium hydroxide, a larger proportion of the anhydride being employed than in the preceding experiment. The compound is slightly soluble in the ordinary solvents; it crystallises in small needles from its concentrated solution in sodium hydrogen carbonate. The *ethyl* ester of the preceding compound is obtained by the oxidation of Zelinsky's ethylphthalic chloride (*Abstr.*, 1887, 669) with an alkaline solution of hydrogen peroxide. The compound crystallises from methyl alcohol in leaflets and melts at $58\text{--}59^\circ$; it is easily soluble in the ordinary solvents with the exception of water and petroleum. A cryoscopic determination of the molecular weight gives numbers agreeing with the double formula $\text{O}_2(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et})_2$.

Diperterephthalic acid, $\text{C}_6\text{H}_4(\text{CO}_3\text{H})_2$, produced by shaking together an ethereal solution of terephthalic chloride and an alkaline solution of hydrogen peroxide, is isolated in the form of its sparingly soluble *monosodium* salt by saturating the product of reaction with carbon dioxide. The salt crystallises in hexagonal plates and explodes on heating or on percussion; it has a neutral reaction and dissolves in sodium hydroxide solution with the formation of a disodium salt. It furnishes white, crystalline precipitates with calcium and barium chlorides, white, amorphous deposits with lead and zinc sulphates, and a light blue, insoluble powder with copper sulphate. The *acid* is obtained in slender, felted needles by acidifying a solution of the disodium salt with dilute sulphuric acid; it is very sparingly soluble, 1 gram requiring 18 litres of cold water; it explodes when heated or on percussion. It is readily converted into terephthalic acid by reducing agents; with manganous salts, it yields a precipitate of the dioxide, whilst aniline is oxidised to nitrosobenzene.

G. T. M.

Derivatives of Gallamic Acid. By ROBERT GNEHM and AUG. W. E. GANSER (*J. pr. Chem.*, 1901, [ii], 63, 77—93).—Gallamide reacts with aminophenyl ethers at $180\text{--}200^\circ$ according to the equation $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{CO}\cdot\text{NH}_2 + \text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OR} =$



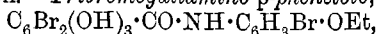
The resulting gallaminophenyl ethers are easily decomposed by alkalis, but are fairly stable in the presence of mineral acids. *Gallaminopphenyl methyl ether* melts at 214° , and the *ethyl* ether at 219° ;

gallamino-o-phenyl methyl ether melts at 238—239°. Gallamide also reacts similarly with aminonaphthyl ethers, but the resulting products are not described.

Gallamide reacts with α - and β -naphthylamines at 180—210° in the same way as with aniline; α -*gallonaphthylamine* crystallises in white needles and melts at 136°. Experiments with *p*-phenylenediamine hydrochloride or benzidine gave crystalline products, which were not further investigated.

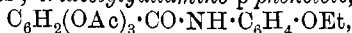
Gallamide is very readily brominated in chloroform solution, with the formation of mono- or di-bromogallamide, according to the quantity of halogen employed. Crystals of these substances deposited from aqueous solution contain water of crystallisation. *Bromogallamide*, $C_6HBr(OH)_3 \cdot CO \cdot NH_2, 1\frac{1}{2}H_2O$, melted at 194—195°, but when anhydrous at 204—205°; *dibromogallamide*, $C_6Br_2(OH)_3 \cdot CO \cdot NH_2, 3\frac{1}{2}H_2O$, melted at 241—243°, but when anhydrous at 245°. Both these substances gave an intense blue colour with ferric chloride, and also with alkalis, although in the latter case the colour changed to red on warming; they were completely decomposed by strong sulphuric acid, but were not altered when boiled with dilute acids.

Gallaminophenyl ethers yield tribromo-derivatives with bromine in chloroform solution. *Tribromogallamino p-phenetole*,



melts at 218—219°, gives a yellowish-green coloration with ferric chloride (soon succeeded, however, by a flocculent precipitate), and is decomposed in the cold by potassium hydroxide.

Gallaminophenyl ethers, when boiled with acetic anhydride, yield triacetyl derivatives; *triacetylgallamino-p-phenetole*,



crystallises from alcohol or toluene in needles, melts at 133—134°, and gives no coloration with ferric chloride. On similarly treating mono- or di-bromogallamide, four acetyl groups are introduced; *tetra-acetyl-bromogallamide*, $C_6HBr(OAc)_3 \cdot CO \cdot NHAc$, melts at 240°, and *tetra-acetyldibromogallamide* at 233°.

Gallamide, gallanilide, and gallaminophenyl ethers react with formaldehyde in presence of hydrogen chloride, in much the same way as does gallic acid itself (compare Möhlau and Kahl, Abstr., 1898, i, 260), forming methylenedigallamides.

A substituted gallamine-blue is obtained by the interaction of gallamino-*p*-phenetole and nitrosodimethylaniline hydrochloride. It is sparingly soluble in water or alcohol, gives a deep blue solution with strong sulphuric acid, a reddish-violet solution with dilute sulphuric acid or alkalis, and a magenta solution with strong hydrochloric acid. Red colouring matters are obtained by the interaction of mono- or di-bromogallamide with nitrosodimethylaniline hydrochloride.

W. A. B.

Synthesis of Aromatic Aldehydes. By ALEXANDR REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 154—157).—By passing a mixture of hydrogen chloride and carbon monoxide through benzene containing freshly prepared aluminium bromide and cuprous chloride in solution, about 85—90 per cent. of the theoretical yield of benz-

aldehyde is obtained. The mechanism of the reaction is thus explained. Hydrogen chloride and aluminium bromide give aluminium chloride and hydrogen bromide, the latter, in the nascent state and in presence of cuprous chloride, then condensing with the carbon monoxide to form the bromoanhydride of formic acid. This bromoanhydride, which readily loses bromine, reacts with benzene, yielding hydrogen bromide and benzaldehyde. T. H. P.

Hydroxynaphthaldehyde or 1-Methanal-2-naphthylol. By R. FOSSE (*Bull. Soc. Chim.*, 1901, [iii], 25, 371—375).—The processes employed by Rousseau and by Kauffmann for the isolation of hydroxynaphthaldehyde from the products of the action of chloroform and sodium hydroxide on β -naphthol are very tedious and unsatisfactory. By working in dilute alcoholic solution, with the precautions described in detail in the paper, the formation of bye-products is reduced to a minimum, and more than 86 per cent. of the theoretical yield of the aldehyde is obtained. Hydroxynaphthaldehyde crystallises from alcohol in prisms and from acetic acid in needles, melts at 77° , and boils at 192° under 27 mm. pressure. The *oxime* crystallises in long, silky needles melting at 157° , and the *phenylhydrazone* forms crystals melting at 195° . With aniline, *o*-toluidine, and *p*-toluidine, hydroxynaphthaldehyde forms yellow, crystalline *hydramides* melting at 87° , 124° , and 132° respectively; the compound with α -naphthylamine crystallises in magnificent, coral-red needles melting at 180° . N. L.

Oxidation of Mesityl Methyl Ketone and the Preparation of Trimethylbenzoic Acid. By L. VAN SCHERPENZEEL (*Rec. Trav. Chim.*, 1900, 19, 377—385).—Claus' method (Abstr., 1890, 981) of oxidising mesityl methyl ketone with 0.4 per cent. aqueous potassium permanganate gives only a poor yield of mesitylgyoxylic acid, but by using a slightly alkaline 3 per cent. solution at 0° (compare Dittrich and Meyer, Abstr., 1891, 1224) good results are obtained; the mesitylgyoxylic acid is best isolated by acidifying with sulphuric acid and extracting with benzene. From the acid solution remaining, mesitylgycollic acid, $C_6H_2Me_3 \cdot CH(OH) \cdot CO_2H$ (m. p. 151 — 152° ; Feith, Abstr., 1892, 329, gives 147° ; methyl ester, m.p. 90 — 91° , Feith gives 92°), can be isolated, its formation being probably due to the action of the alkali, present during the oxidation, on the *aldehyde*, $C_6H_2Me_3 \cdot CO \cdot CHO$, initially formed, a case similar to the transformation by alkalis of glyoxal into glycollic acid. Mesitylgycollic acid is characterised by dissolving in concentrated sulphuric acid with an increasingly red coloration.

The statements of Claus (*loc. cit.*) and of Nass (*Diss. Freiburg*, 1889) concerning the preparation of trimethylbenzoic acid seem to be incorrect; with slightly alkaline 0.75 per cent. aqueous potassium permanganate at the ordinary temperature, mesityl methyl ketone yields principally mesitylgyoxylic acid, which, when separated and left in contact with an amount of the oxidising solution sufficient to form trimethylbenzoic acid, is not further changed beyond yielding a small quantity of an *acid*, $C_{11}H_{10}O_5$, crystallising from water and melting and decomposing at 220 — 222° . This acid fails to yield crystalline salts, and is not apparently the acid $CO_2H \cdot C_6H_2Me_2 \cdot CO \cdot CO_2H$, as it is not

changed either by alkaline potassium permanganate at 60° or by warm nitric acid of sp. gr. 1.1. Mesitylglyoxylic acid is not oxidised by warming with an ammoniacal solution of silver nitrate, but when boiled with dilute nitric acid of sp. gr. 1.1 for several hours, it yields about 24 per cent. of its weight of trimethylbenzoic acid, the principal product being an acid which "may be a dimethylphthalic acid, but is certainly not" the foregoing acid melting at $220-222^{\circ}$. Trimethylbenzoic acid is best prepared by warming mesitylglyoxylic acid with concentrated sulphuric acid.

W. A. D.

Action of Mercaptan on Quinones. By TARBOURIECH (*Bull. Soc. Chim.*, 1901, [iii], 25, 313—315).—The action of ethyl mercaptan on quinone results in the formation of quinol and quinhydrone, the mercaptan being reduced to thioaldehyde, C_2H_4S , but under certain conditions a compound crystallising in large, red needles is obtained, which is formed by the substitution of two S_{Et} groups for two hydrogen atoms in the quinone nucleus. Ethyl mercaptan has no action on anthraquinone or phenanthraquinone, a result which confirms Posner's observation (this vol., i, 14) that only those diketones yield mercaptols which contain carbonyl groups attached to methyl radicles.

N. L.

Chemical Action of Light. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 92—103).—Under the influence of light, quinone and alcohol react, yielding, as was shown by Ciamician (*Abstr.*, 1886, 695), quinol and acetaldehyde. The study of this action of light has now been extended, the following being the results obtained.

*iso*Propyl alcohol and quinone give acetone and quinone, whilst *tert.*butyl alcohol and quinone yield quinol and quinhydrone. Glycerol and quinone give rise to quinhydrone and glycerose, the latter yielding an osazone melting at $136-137^{\circ}$, and not at 131° as stated by Fischer and Tafel (*Abstr.*, 1887, 651). Erythritol and quinone form quinhydrone and erythrose, whilst from *d*-mannitol and quinone are obtained quinhydrone and *d*-mannose. Dulcitol and quinone give a sugar which, with phenylhydrazine, yields the dulcosazone of Fischer and Tafel (*Abstr.*, 1888, 358). In the case of dextrose and quinone, the products are quinhydrone and glucosone.

Thymoquinone and alcohol give acetaldehyde and thymoquinol, the latter melting at 143° , whilst Carstanjen (this Journal, 1871, 351) gave 139.5° . With phenanthraquinone and mannitol, only very slight action takes place.

Quinone has no definite action on lactic, malic, or tartaric acid beyond the evolution of carbon dioxide. With acetic or propionic acid, quinone produces only a gradual darkening, whilst with formic acid it gives quinol and carbon dioxide. The reduction of quinone by benzene is slow, but with the paraffins the action is very rapid and yields products not yet investigated.

The sole products of the reaction between benzophenone and alcohol are acetaldehyde and benzopinacolone. For the last-named

compound, obtained by the reduction of benzophenone by means of zinc and acetic acid, Zagumenny (Abstr., 1881, 813) gave the melting point 168° ; the authors' product melts at 185 — 187° , and that prepared by Zagumenny's method at 186° . Acetophenone is completely converted by the action of alcohol into acetophenonepinacone and isoacetophenonepinacone. Benzaldehyde and alcohol yield hydrobenzoin, isohydrobenzoin, and a resinous polymeride which, when precipitated from benzene solution by the addition of light petroleum, softens at 100 — 101° and has probably the composition $(C_{14}H_{14}O_4)_4$. The action of alcohol on anisaldehyde is slow and gives a small yield of hydroanisoin. Benzoin is oxidised by alcohol with the formation of hydrobenzoin, isohydrobenzoin, and a large proportion of resinous matter, consisting to a small extent of benzoic acid. An alcoholic, ethereal, or acetone solution of vanillin, on exposure to light, gradually deposits crystals of dehydrovanillin. T. H. P.

Action of Nitric Acid on Halogen Derivatives of *p*-Cresol. By THEODOR ZINCKE (*J. pr. Chem.*, 1901, [ii], 63, 183—187. Compare Abstr., 1900, i, 545).—The action of nitric acid on the halogen derivatives of *p*-cresol is shown not to yield oxyketones [ψ -quinols] as stated in the previous paper (*loc. cit.*), but toluquinone derivatives. A wandering of the methyl group to the neighbouring carbon atom has thus taken place in the reaction. Thus 3-bromo-*p*-cresol yields 4:2-bromonitro-*p*-toluquinone, $CO < \begin{smallmatrix} C(NO_2):CMe \\ CBr=CH \end{smallmatrix} > CO$. Probably oxyketones [ψ -quinols] are intermediate products (compare Bamberger, this vol., i, 140), but they have not been isolated.

2:4- (or 4:2-) *Chloronitro-p-toluquinone* forms bright yellow, flattened needles melting and decomposing at 128° . By reduction with tin and hydrochloric acid, *chloroamino-p-toluquinol* is obtained, crystallising in slender needles which melt and decompose at 160 — 162° , and readily oxidise. The *triacetyl* derivative forms long, slender needles melting at 198° .

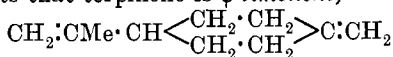
2:4- (or 4:2-) *Bromonitro-p-toluquinone* resembles the chloro-derivative, and melts and decomposes at 135 — 136° . *Bromonitro-p-toluquinol* is obtained from the nitro-compound by reduction with hydriodic acid, and forms long, yellow needles melting at 175° . The *diacetyl* derivative forms colourless, lustrous, four-sided prisms melting at 118° . *Bromo-amino-p-toluquinol* forms needles melting and decomposing at 148 — 149° . The *triacetyl* derivative forms aggregates of needles melting at 203 — 204° .

2:5:4- (or 4:5:2-) *Dibromonitro-p-toluquinone* crystallises in yellow plates or leaflets melting and decomposing at 175 — 180° . *Dibromonitro-p-toluquinol* forms long, silky needles melting at 157 — 158° , and dissolves in alkali carbonate solutions with a deep red colour.

K. J. P. O.

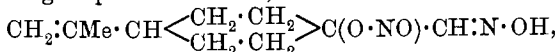
Elimination of Water, Halogen Hydride, and Ammonia in the Terpene Series. By FRIEDRICH W. SEMMLER (*Ber.*, 1901, 34, 708—719).—The author, after discussing the formation of terpinene from terpin, dihydrocarveol, and dihydrocarvylamine, concludes from

the following facts that terpinene is ψ -limonene,

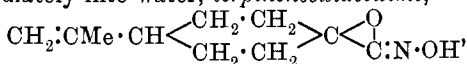


(compare Abstr., 1900, i, 452; and Wallach, *Annalen*, 1893, 277, 146).

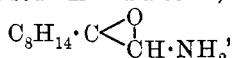
On warming terpinene nitrosite,



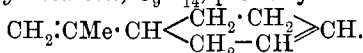
with alcoholic potassium hydroxide, nitrous fumes are evolved, and on pouring immediately into water, *terpineneoxideoxime*,



separates as a white, flocculent mass which melts at about 85°, decomposes when distilled under diminished pressure, and changes when dried in a vacuum into a liquid *isomeride*, although stable when kept in the air. On reduction with sodium and alcohol, the *base*,



boiling at 140–150° under 20 mm. pressure, is obtained. The direct reduction of terpinene nitrosite, on the contrary, yields, in addition to the compounds described by Wallach (this vol., i, 90), a solid *base* melting at 88°, and a *hydrocarbon*, C_8H_{14} , probably



According to the formula given above, terpinene should interact additively with bromine; although, as found by Wallach, this is not the case, its nitrosite combines directly with bromine in glacial acetic acid solution to form, amongst other compounds, a crystalline substance melting at 102°. Von Baeyer found that Beckmann's solution precipitates terpinene (Abstr., 1894, i, 297), and it is now shown that the former is a characteristic reagent for pseudoterpenes or terpene alcohols, for example, sabinene or sabinol.

Carvestrene, boiling at 180–186°, obtained from vestrylamine by the elimination of ammonia, probably contains a quantity of the ψ -form, $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\geq\text{CH}\cdot\text{CMe}:\text{CH}_2$, as the dihydrobromide, when heated $\text{CH}(\text{CH}_2)-\text{CH}$ with quinoline, yields the true ortho-carvestrene boiling at 178°.

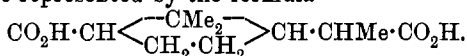
Sabinene, when treated with nitrous acid, fails to yield a definite compound. W. A. D.

Terpenes and Ethereal Oils. Studies in the Fenchone Series. By OTTO WALLACH (*Annalen*, 1901, 315, 273–303. Compare Abstr., 1900, i, 241).—[With WILHELM VON WESTPHALEN.]—The neutral crystalline compound obtained as a bye-product in the preparation of fenchocarboxylic acid from fenchone may be either a pinacene, $\text{C}_{20}\text{H}_{34}\text{O}_2$, or a difenchone, $\text{C}_{20}\text{H}_{32}\text{O}_2$, produced from 2 mols. of the ketone by a condensation similar to that observed in the case of dimethylcyclohexenone (Knoevenagel, Abstr., 1899, i, 340). The substance does not yield well-defined derivatives, and decomposes when heated under reduced pressure at temperatures below 100° into fenchone and an uncrystallisable product. The compound, $\text{C}_{11}\text{H}_{16}\text{O}_2$,

obtained by the dry distillation of lead fenchocarboxylate is in reality

an ortho-diketone, $\text{CH} \begin{array}{c} \text{CO} \cdot \text{CO} \cdot \text{CHMe} \\ \text{CMe}_2 \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} \text{CH}$, and not an ortho-hydr-

oxyketone, as previously suggested (Abstr., 1898, i, 487); it is accordingly termed *carbofenchonone* instead of hydroxycarbofenchonone. The *alcohol*, $\text{C}_{11}\text{H}_{18}\text{O}_2$, formed by the action of zinc dust and acetic acid on the diketone, crystallises from dilute alcohol and melts at 89° . Carbofenchone, on oxidation, yields a dicarboxylic *acid*, $\text{C}_{11}\text{H}_{18}\text{O}_4$, which melts at $172\text{--}173^\circ$. Its constitution, assuming that of the diketone, may be represented by the formula



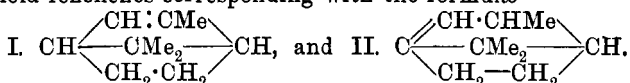
Crude fenchonitrile, obtained by warming fenchonoxime with dilute sulphuric acid, consists of two isomerides, which behave differently towards sodium ethoxide, the one yielding an amide, whilst the other is completely hydrolysed and furnishes solid fencholenic acid, a compound crystallising from acetone or light petroleum and melting at $68\text{--}70^\circ$ (compare Cockburn, Trans., 1899, 75, 501). The liquid and solid modifications of fencholenic acid are designated by the symbols α and β respectively. Both α - and β -acids yield brominated lactones by the action of sodium hypobromite on cold solutions of their sodium salts, these derivatives melting respectively at 76° and 80° . β -Fencholenamide melts at $85\text{--}86^\circ$, the melting point of its isomeride being $113\text{--}114^\circ$.

[With EDGAR NEUMANN.]—A strongly laevorotatory fenchyl chloride is produced by mixing together at low temperatures in light petroleum, phosphorus pentachloride and pure *Dl*-fenchyl alcohol, removing the phosphorus oxychloride produced with cold water, and distilling the dried residue in a vacuum. The hydrocarbon obtained by the action of aniline on this chloride consists chiefly of *Dl*-fenchene. When the reagents are mixed without cooling, and the action completed on the water-bath, a dextrorotatory fenchyl chloride is produced, and this yields a fenchene having a rotation of the same sign.

The *ether*, $\text{C}_{10}\text{H}_7 \cdot \text{OEt}$, produced by heating *Dd*-fenchene with alcoholic sulphuric acid, boils at $200\text{--}201^\circ$, and on treatment with metallic sodium yields the sodium derivative of the alcohol, $\text{C}_{10}\text{H}_{17} \cdot \text{OH}$. This alcohol melts at 61° , and is identical with the *isofenchyl* alcohol discovered by Bertram and Helle (compare Abstr., 1900, i, 398). Different specimens of crude fenchene vary greatly in their behaviour towards permanganate solution, and generally yield a mixture of *Dl*- and *Dd*-hydroxyfenchenic acids, the laevorotatory isomeride predominating. Some samples of the hydrocarbon contain readily oxidisable substances, and in this case the product of oxidation is a complex mixture consisting of the two hydroxyfenchenic acids, together with acids of the acetic series and a *ketonic acid*, $\text{C}_8\text{H}_{12}\text{O}_3$, this compound being identified by means of its *semicarbazone*, $\text{C}_8\text{H}_{12}\text{O}_2 \cdot \text{CON}_3\text{H}_3$, and its *silver salt*, $\text{C}_8\text{H}_{11}\text{O}_3\text{Ag}$.

Fenchyl alcohol, $\text{CH} \begin{array}{c} \text{CH(OH)} \cdot \text{CHMe} \\ \text{CMe}_2 \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} \text{CH}$, should, on dehydra-

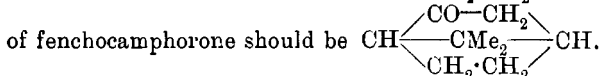
tion, yield fenchenes corresponding with the formulæ



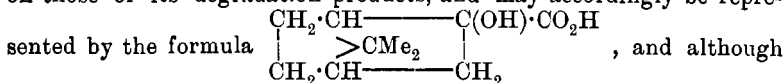
The latter of these would on oxidation give rise to the ketonic acids, $\text{CO} \begin{array}{c} \diagup \text{CMe}_2 \diagdown \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \diagup \end{array} \text{CH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ and $\text{CO} \begin{array}{c} \diagup \text{CMe}_2 \diagdown \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \diagup \end{array} \text{CH} \cdot \text{CO}_2\text{H}$, and the acid, $\text{C}_8\text{H}_{12}\text{O}_3$, isolated from the products of oxidation, may possibly have the constitution represented by the second of these formulæ.

The *acetyl* derivative of *Dl*-hydroxyfenchenic acid melts at $109-110^\circ$; the acid itself on oxidation yields *Dd*-fenchocamphorone (Abstr., 1899, i, 488; 1900, i, 241). This substance, when reduced with sodium in ethereal solution, gives rise to fenchocamphorol and the corresponding *pinacone*, $\text{C}_{18}\text{H}_{30}\text{O}_2$, melting at $192-193^\circ$.

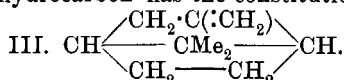
On reducing the fenchocamphornitrile with sodium and alcohol, the base $\text{C}_9\text{H}_{15} \cdot \text{NH}_2$ is obtained, and is identified by means of its platinum-chloride and carbamide. An isomeric *base*, produced by the direct reduction of fenchocamphoronoxyime with sodium and amyl alcohol, boils at $196-199^\circ$, and solidifies at low temperatures. Its *hydrochloride*, $\text{C}_9\text{H}_{15} \cdot \text{NH}_2 \cdot \text{HCl}$, is very stable, and crystallises from a mixture of ether and alcohol. The acid, $\text{C}_9\text{H}_{14}\text{O}_4$, produced by oxidising fenchocamphorone with nitric acid, yields the *anhydride*, $\text{C}_9\text{H}_{12}\text{O}_3$, and the *monoanilide*, melting respectively at $176-177^\circ$ and 211° . These compounds agree in their properties with the corresponding derivatives of camphopyric acid (compare Marsh and Gardner, Trans., 1896, 69, 74) and hence the two acids are identical. Assuming that camphopyric acid has the constitution $\text{HO}_2\text{C} \cdot \text{CH} \begin{array}{c} \diagup \text{CMe}_2 \diagdown \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \diagup \end{array} \text{CH} \cdot \text{CO}_2\text{H}$, then that



The constitution of *Dl*-hydroxyfenchenic acid (m. p. 152°) depends on those of its degradation products, and may accordingly be represented by the formula



such a substance may be considered as a derivative of the fenchene of formula I, yet its formation is more readily explained on the assumption that the hydrocarbon has the constitution



This hydrocarbon could only be formed from fenchyl alcohol if a shifting of the double linking in formulæ I and II occurs; if this possibility be admitted, then four other structurally dissimilar fenchenes are theoretically possible.

Dd-Hydroxyfenchenic acid (m. p. 138°) yields an *acetyl* derivative crystallising in prisms and melting at $122-124^\circ$.

Dl-Fenchocamphorone forms an oxime and a nitrile like its *Dd*-isomeride, but differs from this substance in not yielding a camphopyric

acid with dilute nitric acid. The principal product of this action is an acid whose mono- and di-anilides agree in properties with those of *as*-dimethylsuccinic acid; there is, however, a discrepancy in the melting points of the anhydrides, that from the acid derived from *Dl*-fenchocamphorone melting at 125–130°, whilst *as* dimethylsuccinic anhydride melts at 29°.

Since *Dd*-fenchene also yields a hydroxyfenchenic acid, it may be a stereoisomeride of *Dl* fenchene; on the other hand, the two fenchocamphorones behave quite differently on oxidation with nitric acid, and, moreover, the hydrocarbons themselves are not attacked with equal readiness by permanganate solutions, so that it is quite possible that the two isomerides may be structurally dissimilar. G. T. M.

Ethereal Oil of Buchu Leaves, and the Constitution of its Constituents. By IWAN KONDAKOFF and N. BACHTSCHÉEFF (*J. pr. Chem.*, 1901, [ii], 63, 49–77. Compare Bialobrzezski, Abstr., 1897, i, 433).—The best samples of oil from *Barosma betulina* and *B. serratifolia* contain about 10 per cent. of hydrocarbons, $C_{10}H_{16}$, 60 per cent. of a ketomenthone, $C_{10}H_{18}O$, and 5 per cent. of diosphenol.

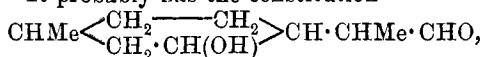
The fraction comprising the hydrocarbons contained neither sylvestrene nor carvestrene, and its boiling point is higher than that of phellandrene. On brominating it in the cold, and afterwards fractionally crystallising the product from alcohol-ether, tetrabromides were obtained indicating the presence of *d*-limonene and dipentene in the original oil.

The ketomenthone, $C_{10}H_{18}O$, is a colourless liquid with a peppermint-like odour; it boils at 208·5–209·5° under 760 mm. pressure, and has a sp. gr. 0·9004 at 19°/19°, $[\alpha]_D - 16^{\circ}6'$, $n_D 1\cdot45359$, and molecular refraction 46·28. Its oxime is liquid and optically active. On reduction with sodium in methyl alcoholic solution, it yielded a solid and a liquid *menthol*. The former crystallised in needles, melted at 38·5–39°, had a sp. gr. 0·9006 at 32°/32°, and $n_D 1\cdot45869$ at 32°, and dissolved in all organic solvents. The *benzoate* melted at 82°; when treated with phosphoric oxide, this menthol was converted into a menthene which boiled at 166·5–168·5° under 785 mm. pressure, and had a sp. gr. 0·8112 at 19°/19°, $n_D 1\cdot45109$ and $[\alpha]_D - 13^{\circ}46'$. The isomeric liquid menthol boiled at 106·5–109° under 18 mm. pressure, had a sp. gr. 0·9041 at 21·6°/21·6°, $[\alpha]_D + 26^{\circ}30'$ and $n_D 1\cdot461793$, and gave a menthene of lower levorotation than that described by Berkenheim (Abstr., 1892, 866), or Masson and Reyckler (*Ber.*, 1896, 29, 1843). The solid menthol is not identical with the natural substance, and the liquid isomeride seems to be new.

Diosphenol, $C_{10}H_{18}O_2$, or $C_{10}H_{16}O_2$, an inactive phenolic aldehyde, melted at 82°. On reduction with hydriodic acid and phosphorus at 210°, it yielded a hydrocarbon, $C_{10}H_{20}$, of the hexahydrocymene series; this boiled at 165–168° under 762 mm. pressure, had a sp. gr. 0·7916 at 21·6°/21·6°, and $n_D 1\cdot43539$. On reduction with sodium and alcohol, it gave (1) an inactive *menthol*, which was volatile with steam, boiled at 215–216° under 763 mm. pressure, and had a sp. gr. 0·9052 at 20°/20° and $n_D 1\cdot464456$. The inactive *iodide* obtained from this menthol boiled at 126·5° under 17 mm. pressure, and with alcoholic potassium

hydroxide yielded an active *menthene*, which boiled at 168—169°, and had a sp. gr. 0.8158 at 19.8°/19.8°, n_D 1.45909 and $[\alpha]_D - 37'$. (2) An active, odourless *glycol*, $C_{10}H_{20}O_2$, which crystallised in colourless needles, melted at 92°, had a sharp, cooling taste, and was not volatile with steam. When heated with hydriodic acid at 100° for 6 hours, it yielded a liquid *menthyl iodide*, $C_{10}H_{19}I$, which boiled at 112—114° under 9 mm. pressure, and had a sp. gr. 1.359 at 20.6°/20.6° and n_D 1.520771. With hydriodic acid at 185°, it yielded the same hexahydrocymene as does diosphenol itself. (3) A liquid *glycol*, stereoisomeric with the preceding compound; it boiled at 141.5—145° under 13 mm. pressure, and had a sp. gr. 0.995 at 21.6°/21.6°, and n_D 1.47877.

Diosphenol, when heated with phosphoric oxide, yields propylene and *m*-cresol. It probably has the constitution



or $CHMe \left\langle \begin{array}{c} CH_2 - CH_2 \\ CH_2 \cdot C(OH) \end{array} \right\rangle C \cdot CHMe \cdot CHO$, and the glycol derived from

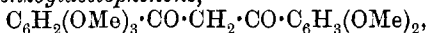
it will be $CHMe \left\langle \begin{array}{c} CH_2 - CH_2 \\ CH_2 \cdot CH(OH) \end{array} \right\rangle CH \cdot CHMe \cdot CH_2 \cdot OH$. With regard to the constitution of the other constituents of buchu oil, the authors suggest that the hydrocarbon is $CMe \left\langle \begin{array}{c} CH - CH_2 \\ CH_2 \cdot CH_2 \end{array} \right\rangle CH \cdot CMe \cdot CH_2$, and

the ketomenthone, $CHMe \left\langle \begin{array}{c} CH_2 \cdot CH_2 \\ CH_2 - CO \end{array} \right\rangle CH \cdot CHMe_2$. W. A. B.

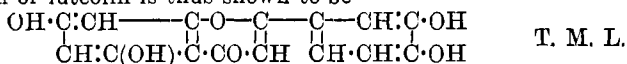
Constitution of Gallotannin. By HENRI POTTEVIN (*Compt. rend.*, 1901, 132, 704—706).—Commercial gallotannin when purified by ether extraction consists essentially of a glucoside of gallic acid; it yields this acid and dextrose when hydrolysed by tannase, and when heated at 110° in a sealed tube with very dilute hydrochloric acid it yields the same sugar and digallic acid (compare this vol., i, 179).

G. T. M.

Synthesis of Luteolin. By STANISLAUS VON KOSTANECKI (*Bull. Soc. Ind. Mulh.*, 1901, 71, 35—41).—By the action of ethyl veratrate, $C_6H_5(OMe)_2 \cdot CO_2Et$, on *s*-trimethoxyacetophenone, $C_6H_2(OMe)_3 \cdot CO \cdot CH_3$, a *pentamethoxybenzoylacetophenone*,



is produced, which is converted into luteolin by heating with hydriodic acid, when five methyl groups and a mol. of water are eliminated. The constitution of luteolin is thus shown to be



T. M. L.

Bromo-derivatives of Coumarone. By HUGO SIMONIS (*Ber.*, 1901, 34, 781—784).—The tribromocoumarone produced by the action of bromine on 1:2-dibromocoumarone (Stoermer, *Abstr.*, 1901, i, 654) is not the 1:2:4-compound, but is probably the 1:2:6-isomeride.

1:2:4-Tribromocoumarone, $C_6H_3Br \left\langle \begin{array}{c} CBr \\ O \end{array} \right\rangle CBr$, prepared by the action of bromine on 1:4-dibromocoumarone dissolved in carbon disulphide, crystallises in needles and melts at 115°. 1:2:4:6-Tetra-

bromocoumarone, $C_6H_2Br_2 \begin{smallmatrix} \diagup CBr \\ O \\ \diagdown CBr \end{smallmatrix}$, prepared by the slow action of bromine on 1:4:6-tribromocoumarone, crystallises in white needles and melts at 134° . T. M. L.

Coumarilic Acid and its Derivatives. By RICHARD STOERMER and G. CALOV (*Ber.*, 1901, 34, 770—775).—The chief product of the action of bromine on coumarilic acid is Stoermer and Richter's tribromocoumarone (*Abstr.*, 1900, i, 654), and a pure monobromocoumarone could not be isolated. The *amide*, $C_9H_7O_2N$, prepared by the action of ammonia on the ethyl ester, forms white flakes and melts at 159° . The *nitrile*, C_9H_5ON , crystallises from dilute alcohol in long, silky needles, melts at 36° , and smells like cinnamon. The acid *chloride* melts at 52° , smells like bitter almond oil, and is decomposed by warming with water. The *phenyl ester*, $C_{15}H_{10}O_3$, crystallises from alcohol in long, white needles and melts at 101° . The *anilide* forms small, yellowish-white needles and melts at 159° . The *hydrazide*, $C_9H_8O_2N_2$, crystallises from dilute alcohol in white, felted needles, melts at 172° , and reduces Fehling's solution and ammoniacal silver nitrate. The *azoimide*, $C_9H_6O_2N_3$, crystallises from dilute alcohol in small, white flakes and melts at 109° . *Urethylcoumarone*, $C_9H_6O \cdot NH \cdot CO_2Et$, prepared by boiling the azoimide with alcohol, crystallises from alcohol in large, glistening, white scales and melts at 141° ; it is hydrolysed by hydrogen chloride and by potassium hydroxide to *o*-hydroxyphenylacetic acid.

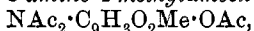
Acetylcoumaroneoxime, $C_{10}H_9O_2N$, crystallises from dilute alcohol in white, silky needles and melts at 150° . *Dicoumarylketoxime*, $C_{17}H_{11}O_3N$, forms yellowish-white, felted needles, and melts and decomposes at 222 — 223° . Neither of these compounds undergoes isomeric change smoothly when acted on by phosphorus pentachloride. T. M. L.

Derivatives of 4-Methylumbelliferone. By HANS VON PECHMANN and JULIUS OBERMILLER (*Ber.*, 1901, 34, 660—674).—8-Nitro-4-methylumbelliferone,
$$\begin{array}{c} CH:CH-C \cdot CMe:CH \\ | \\ OH \cdot C \cdot C(NO_2) \cdot C-O-CO \end{array}$$
 (von Pechmann and Cohen,

Abstr., 1884, 1331), is obtained by dissolving crude 4-methylumbelliferone in strong sulphuric acid, and nitrating it below 0° with a mixture of strong nitric and sulphuric acids. When crystallised from nitrobenzene, it melts at 228 — 229° , from a mixture of nitrobenzene and alcohol (2:1) at 255° . When heated with strong ammonia at 80 — 85° , it yields 2-nitroresorcinol, the yellowish *dibenzoyl* derivative of which melts at 138 — 139° . It is reduced by stannous chloride and alcoholic hydrochloric acid to yellow 8-amino-4-methylumbelliferone, which decomposes and melts completely below 270° . Nitrous acid converts this amino-compound, at 0 — 5° and in the dark, into 4-methylumbelliferone-8-diazoanhydride, $N \leq \begin{smallmatrix} O \\ N \end{smallmatrix} > C_9H_8O_2Me$, which was mistaken by von Pechmann and Cohen for a nitroso-derivative. It forms yellowish-red crystals, and perhaps exists in two varieties decomposing at 173 — 175° and 135 — 136° respectively; the corresponding *picrates* are red, and melt at 176 — 180° and 160 — 165° . It is stable in the dark, but

not in the light; it unites with phenols, but not with dimethylaniline, forming azo-dyes; it yields a *hydrochloride*, and with potassium sulphite it forms *potassium-4-methylumbelliferone-8-diazosulphonate*, which is red, and crystallises with $2\text{H}_2\text{O}$; the solution of the hydrochloride yields the diazoanhydride when it is precipitated with sodium carbonate or acetate, 4-methylumbelliferone when it is heated with copper powder, and 8-hydrazino-4-methylumbelliferone when it is reduced with stannous chloride.

When the amino-compound is heated with acetic anhydride and sodium acetate, *triacetyl-8-amino-4-methylumbelliferone*,



melting at $183\text{--}184^\circ$ is obtained. When this is dissolved in alcoholic potash and then precipitated with hydrochloric acid, the *diacetyl* compound, $\text{N}(\text{Ac})_2 \cdot \text{C}_9\text{H}_3\text{O}_2\text{Me} \cdot \text{OH}$, melting at $261\text{--}262^\circ$ is formed. This is hydrolysed by cold, strong hydrochloric acid to the *monoacetyl* compound, $\text{NHAc} \cdot \text{C}_9\text{H}_3\text{O}_2\text{MeOH}$, melting at 290° , whilst the hot acid hydrolyses it to 8-amino-4-methylumbelliferone. These acetyl derivatives lose acetic anhydride, acetic acid, or water respectively when heated, and in addition form *ethenyl-8-amino-4-methylumbelliferone*, $\text{CMe} \begin{smallmatrix} \text{O} \\ \diagup \text{N} \diagdown \end{smallmatrix} \text{C}_9\text{H}_3\text{O}_2\text{Me}$, which melts at $202\text{--}203^\circ$, and readily regenerates the monoacetyl compound under the influence of hydrochloric acid. By boiling nitromethylumbelliferone with acetic anhydride and sodium acetate, *8-nitro-4-methylumbelliferone acetate*, $\text{NO}_2 \cdot \text{C}_9\text{H}_3\text{O}_2\text{Me} \cdot \text{OAc}$, melting at $165\text{--}166^\circ$, is obtained. Reduction of this with stannous chloride does not give the expected aminohydroxy-compound; the monoacetyl-amino-compound described above is obtained instead, and by very careful work the ethenyl-amino-compound can be isolated as an intermediate product.

8-Nitro-4-methylumbelliferone methyl ether, $\text{NO}_2 \cdot \text{C}_9\text{H}_3\text{O}_2\text{Me} \cdot \text{OMe}$, is obtained by heating nitroumbelliferone with methyl-alcoholic sodium methoxide and methyl iodide at 100° ; it is yellowish, melts at 230° , and can be reduced with stannous chloride and hydrochloric acid to yellowish *8-amino-4-methylumbelliferone methyl ether*, which melts at 161° .

When β -methylumbelliferone methyl ether (von Pechmann and Duisberg, Abstr., 1884, 66) is nitrated in the manner already given, in addition to the methyl ether just described there is obtained an isomeride which is less soluble in a mixture of nitrobenzene and alcohol, is pale yellow, and melts at $281\text{--}282^\circ$. This is probably 6-nitro-

4-methylumbelliferone methyl ether, $\begin{smallmatrix} \text{C}(\text{NO}_2) \cdot \text{CH} \cdot \text{C} \cdot \text{CMe} \cdot \text{CH} \\ \text{C}(\text{OMe}) \cdot \text{CH} \cdot \text{C} \cdot \text{O} \cdot \text{CO} \end{smallmatrix}$; when reduced, it yields *6-amino-4-methylumbelliferone methyl ether*, which melts at $221\text{--}222^\circ$.
C. F. B.

Arylthiosulphonates of Organic Bases. By JULIUS TROEGER and OTTO LINDE (*Arch. Pharm.*, 1901, 239, 121—145).—Attention is drawn to the close analogy between arylthiosulphonates and thiosulphates, to which the former stand in the same relation as the arylsulphinates to the sulphites. A number of arylthiosulphonates of

organic bases, chiefly alkaloids, is described. These were prepared by mixing aqueous solutions of the potassium arylthiosulphonate and a salt (usually the hydrochloride) of the base; they separated sometimes in crystals, but more often as oils, which usually solidified after a time. The salts prepared are enumerated below; when they were analysed their composition is given, B standing for 1 mol. of the base, A for 1 mol. of the acid, $C_6H_5 \cdot SO_2 \cdot SH$, $C_7H_7 \cdot SO_2 \cdot SH$, or $C_{10}H_7 \cdot SO_2 \cdot SH$, as the case may be. Benzidine *p*-toluenethiosulphonate forms a noteworthy exception to the general rule, as it contains only 1 mol. of acid per 1 mol. of the di-acid base.

| | Benzene- thio- sulphonate. | <i>p</i> -Tolu- enethio- sulphonate. | α -Naphthal- enethio- sulphonate. | β -Naph- thalenethio- sulphonate. |
|---|----------------------------------|--|--|---|
| Berberine, $C_{20}H_{17}O_4N$ | B,A | B,A, H_2O | B,A | B,A |
| Brucine, $C_{23}H_{26}O_4N_2$ | B,A | B,A | B,A | B,A |
| Strychnine, $C_{21}H_{22}O_2N_2$ | B,A | B,A | B,A | B,A |
| Morphine, $C_{17}H_{19}O_3N$ | B,A | B,A | B,A | B,A |
| Codeine, $C_{18}H_{21}O_3N$ | — | B,A | B,A | B,A |
| Cinchonine, $C_{19}H_{22}ON_2$ | — | B,A | — | B,A |
| Cinchonidine, $C_{19}H_{22}ON_2$ | — | — | B,A | — |
| Quinine, $C_{20}H_{24}O_2N_2$ | — | B,A | — | — |
| Quinidine, $C_{20}H_{24}O_2N_2$ | — | — | — | B,A |
| Guanidine, CH_5N_3 | B,A | B,A | B,A | B,A |
| Aniline, C_6H_7N | — | B,A | — | B,A |
| Phenylhydrazine, $C_6H_8N_2$ | — | — | B,A | B,A |
| <i>m</i> -Phenylenediamine, $C_6H_8N_2$ | — | B,2A | — | B,2A |
| <i>p</i> -Phenylenediamine, $C_6H_8N_2$ | B,2A | B,2A | B,2A | B,2A |
| Benzidine, $C_{12}H_{12}N_2$ | B,2A | B,A | B,2A | B,2A |
| Tolidine, $C_{14}H_{16}N_2$ | B,2A | B,2A | B,2A | B,2A |

C. F. B.

Cinchonine. By ÉMILE JUNGFLAISCH and EUGÈNE LÉGER (*Compt. rend.*, 1901, 132, 828—830. Compare this vol., i, 287).—Specimens of crude basic cinchonine sulphate always contain notable quantities of the hydrocinchonine salt, sometimes to the extent of 20 per cent. The latter base is only slowly eliminated by fractional crystallisation of the normal salt from 95 per cent. alcohol, each crystallisation removing one quarter of the hydrocinchonine salt present in the material. A specimen of cinchonine sulphate containing only 1 per cent. of the hydrocinchonine salt is less soluble in water at different temperatures than the salt of the crude mixture of bases. Purified cinchonine melts at 264.3° the melting points of specimens of the crude base varying from 248 to 268.8° ; it has a greater optical activity than a mixture of the two alkaloids, hydrocinchonine being less active than cinchonine and having $[\alpha]_D 229.6^\circ$. G. T. M.

Echinopsine a new Crystalline Alkaloid. By MAURITS GRESHOFF (*Rec. Trav. Chim.*, 1900, 19, 360—363).—*Echinopsine*, $C_{11}H_9ON$, is present in 15 different species of the genus *Echinops*, and is best obtained from the seeds of *Echinops Ritro*, L., by removing their oil with light petroleum and then extracting with alcohol; it dissolves

in 60 parts of water at 15° , in 6 at 100° , crystallises with $1\text{H}_2\text{O}$ in rhombs, or when anhydrous, in tufts of needles. It melts at 152° and does not decompose at 350° . The *hydrochloride*, $\text{C}_{11}\text{H}_9\text{ON}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$, forms large, rhombic crystals; the *sulphate*, with either 2 or 8 H_2O , forms long needles, and the *nitrate* contains $3\text{H}_2\text{O}$; the *oxalate*, with $4\text{H}_2\text{O}$, forms good crystals, and the *picrate* melts at 215° . The *mercurichloride* melts at 204° and the *mercuriodide* at 178° ; with a solution of iodine, a crystalline compound is formed, which melts at about 135° , and can be used to localise the alkaloid in the tissues of *Echinops*. The toxic action of the alkaloid is similar to, but not identical with, that of a mixture of strychnine and brucine. Its composition is that of a phenylpyridone, but it is not identical with any known phenylpyridone; on reduction with zinc dust in a stream of hydrogen, it yields an *amine* with an odour of pyridine, but not identical with any of the known phenylpyridines. Fused with potash, it yields ammonia and pyridine.

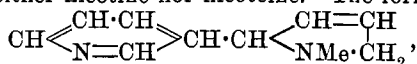
The following compounds are also present in *Echinops*: β -*echinopsine* which melts at 135° , and *echinopsfluorescein*, of which traces only were isolated.

W. A. D.

New Alkaloids from Tobacco. By AMÉ PICTET and A. RORSCHY (*Ber.*, 1901, 34, 696—708).—The crude nicotine obtained by distilling a concentrated aqueous extract of tobacco leaves with steam, contains about 0.5 per cent. of its weight of an isomeride, *nicotimine*, $\text{C}_{10}\text{H}_{14}\text{N}_2$; this is a secondary base and is separated by converting it into its *nitroso*-derivative, removing the nicotine by distillation under diminished pressure, boiling the residue with concentrated hydrochloric acid, and converting the regenerated base into its *benzoyl* derivative. The latter is a bright yellow oil which boils above 350° , does not solidify at -10° , and on hydrolysis with concentrated hydrochloric acid yields nicotimine as a colourless liquid boiling at 250 — 255° . The base is easily soluble in water, is volatile with steam, and yields a white, crystalline, deliquescent *hydrochloride*; the yellow *platinichloride* becomes greyish at 270° , but does not melt at 290° ; the *aurichloride* decomposes at 182 — 185° , the *mercurichloride* at 190° , whilst the *picrate* forms thick prisms and melts at 163° . These facts show that nicotimine is not identical with Pinner's metanictine (*Abstr.*, 1894, i, 388).

The aqueous extract remaining after the removal of the nicotine and its isomeride contains two alkaloids, nicotine and nicotelline, which are not volatile with steam. *Nicotine*, $\text{C}_{10}\text{H}_{12}\text{N}_2$, is a colourless liquid which is readily soluble in water and in ether, boils at 266 — 267° (uncorr.), and does not solidify at -79° ; it has a sp. gr. 1.0778° at $12.5^{\circ}/4^{\circ}$, n_D 1.56021 at 14° , a mol. refraction 48.01 , and $[\alpha]_D$ -46.41° . The *dihydrochloride*, is amorphous and has $[\alpha]_D$ -8.27° ; the *platinichloride*, $\text{C}_{10}\text{H}_{12}\text{N}_2\cdot\text{H}_2\text{PtCl}_6$, forms yellow crystals and does not melt at 280° , the *aurichloride* becomes grey at 150° and melts and decomposes at 186° , and the *picrate* forms large, transparent prisms and melts at 165° ; two *mercurichlorides* are described, one melting at about 115° and the other at 215° with decomposition. The *dimethiodide*, $\text{C}_{10}\text{H}_{12}\text{N}_2\cdot 2\text{MeI}$, is a yellow oil which cannot be made to crystallise. Attempts to

convert nicotine into nicotine by reduction failed; tin and hydrochloric acid are without action, whilst sodium and alcohol yield a product which is not volatile with steam. When the *bromo*-derivative of the base is reduced by tin and hydrochloric acid (compare Abstr., 1898, i, 688, and 1900, i, 685), a base is obtained which is volatile with steam but is neither nicotine nor nicotine. The formula



given to the base shows it to be closely allied with dihydronicotyrine (Pictet and Crépieux, Abstr., 1898, i, 688) and dehydronicotine (Pinner and Wolfenstein, Abstr., 1892, 1010; 1895, ii, 308), and explains the following facts. (1) Nicotine on oxidation with nitric acid yields nicotinic acid; (2) it decolorises aqueous potassium permanganate in presence of sulphuric acid; (3) its acid solutions respond to the tests for a pyrrole derivative.

Nicotelline, $\text{C}_{10}\text{H}_8\text{N}_2$, is only very slightly soluble in water and ether, and is best extracted from the original aqueous solution by chloroform; it crystallises from this solvent on adding light petroleum in small, white needles, melts at $147-148^\circ$ and boils slightly above 300° ; unlike the other alkaloids of tobacco, its aqueous solution is neutral to litmus. It does not appear to be a pyrrole derivative, and does not decolorise potassium permanganate in presence of sulphuric acid; the *hydrochloride* is easily soluble in water and the *platinichloride* sparingly so; the *aurichloride* sinters and decomposes at about 170° , and the *mercurichloride* melts at $200-201^\circ$. Nicotelline differs from the other alkaloids of tobacco in yielding a very sparingly soluble *dichromate*.
W. A. D.

Pilocarpine. By ADOLF PINNER and ERICH KOHLHAMMER (*Ber.*, 1901, **34**, 727—736. Compare Abstr., 1900, i, 456, 685, and Jowett, *Trans.*, 1900, **77**, 494, 851, and Abstr., i, 686).—The authors confirm their statement that the potassium and barium salts of piluvic acid are derived from an acid $\text{C}_8\text{H}_{14}\text{O}_6$, although the *acid* itself, a yellowish, non-crystallisable syrup, has the formula $\text{C}_8\text{H}_{12}\text{O}_5$, and the ethyl ester the formula $\text{C}_8\text{H}_{10}\text{O}_5\text{Et}_2$; the *amyl* ester, $\text{C}_8\text{H}_{10}\text{O}_5(\text{C}_5\text{H}_{11})_2$ boils at 192° under 25 mm. pressure and is somewhat unstable.

In addition to piluvic acid, the oxidation of pilocarpine with aqueous potassium permanganate apparently gives rise to nitrogenous acids, a small quantity of *barium* salt, $\text{C}_{11}\text{H}_{15}\text{O}_5\text{NBa}$ being isolated.

When barium pilocarpeate is oxidised with 1 per cent. aqueous potassium permanganate (corresponding with 50), it yields *isohydrochelidonic acid*, $\text{C}_7\text{H}_{10}\text{O}_5$, which crystallises from its aqueous solution in colourless, lustrous needles and melts at 145° ; the *barium* salt, $\text{C}_7\text{H}_8\text{O}_5\text{Ba} \cdot \text{H}_2\text{O}$, forms small leaflets and is sparingly soluble, and the *lead* salt, $\text{C}_7\text{H}_8\text{O}_5\text{Pb}$, is anhydrous. Whether the acid is identical with Volhard's hydrochelidonic acid (Abstr., 1890, 30; 1892, 432) is uncertain; the melting point is the same, but Volhard's barium salt contained $2-2\frac{1}{2}\text{H}_2\text{O}$. In addition to the *isohydrochelidonic acid* isolated, a potassium salt was obtained which was either potassium malonate or a molecular mixture of potassium oxalate and succinate.

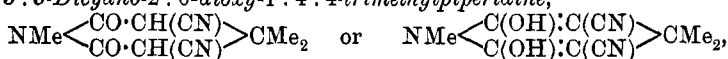
W. A. D.

Thebenidine. By EDUARD VONGERICHTEN (*Ber.*, 1901, 34, 767—770).—The base *thebenidine*, which is produced together with pyrene on distilling thebenine with zinc dust, is insoluble in water, but crystallises from benzene, melts at 144—148°, and is not oxidised by chromic acid; it forms a yellow *platinichloride*, $(C_{15}H_9N)_2 \cdot H_2PtCl_6$; the *methiodide*, $C_{16}H_{12}NI$, forms yellow prisms, melts at about 240° and cannot be methylated further. The formula $C_6H_3 \begin{smallmatrix} \text{CH}=\text{N} \\ \text{CH}:\text{CH} \end{smallmatrix} C_6H_3$ is suggested for the base. T. M. L.

Theobromine and Caffeine and the Salts they Form. By THEODOR PAUL (*Arch. Pharm.*, 1901, 239, 48—90).—One part of theobromine requires for its solution 3282 parts of (carefully purified) water at 18°; of *N*/4 hydrochloric acid, 2125; of *N* hydrochloric acid, 1205; of *N*/10 sodium hydroxide, 57·02; of *N*/4 sodium hydroxide, 22·93 parts. As the solubility in acid is so very little more than in water, it is evident that the hydrochloride is very largely dissociated hydrolytically, and that the basic character of theobromine is very feeble. On the other hand, the large increase of solubility in sodium hydroxide indicates that the sodium salt is much less dissociated hydrolytically, and that the acid character of theobromine is much more marked than the basic. The dissociation constant, *k*, of theobromine for its dissociation into $C_7H_8O_2N_4 \cdot OH$ and \bar{H} , is $1\cdot33 \times 10^{-8}$, and the degree of its dissociation in the solution saturated at 18° is 0·0027. The constant for its dissociation into $C_7H_8O_2N_4 \cdot H$ and \bar{OH} is $1\cdot5 \times 10^{-14}$. As an acid, then, theobromine is about of equal strength with the substituted phenols and the cresols, and is about 100 times weaker than uric acid. As a base, it is about 60 times weaker than betaine, and about 40,000 times weaker than aniline. The molecular conductivity of theobromine in aqueous solution saturated at 18°, is 0·9; it may be regarded as due only to the acid dissociation of the substance. C. F. B.

Synthesis of Derivatives of Pyridine and of Trimethylene-pyrrole. By ICILIO GUARESCHI (*Mem. Real. Accad. Sci. Torino*, 1901, [ii], 50, 235—288. Compare *Abstr.*, 1897, i, 168; Grande, *Abstr.*, 1898, i, 272; Quenda, *Abstr.*, 1898, i, 272; Pasquali, *Abstr.*, 1898, i, 272; Sabbatani, *Abstr.*, 1898, i, 273; Guareschi, *Abstr.*, 1898, i, 274; 1900, i, 52, and 558; Guareschi and Grande, *Abstr.*, 1900, i, 111 and 112).—This paper deals with the formation of ring compounds by the action of various ketones on ethyl cyanoacetate in presence of either ammonia or an amine. In addition to the work already published (*loc. cit.*), the following new results have been obtained.

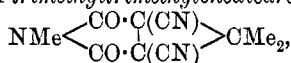
3:5-Dicyano-2:6-dioxy-1:4:4-trimethylpiperidine,



prepared by the interaction of acetone (1 mol.), methyl or ethyl cyanoacetate (2 mols.) and an alcoholic solution of methylamine (3 mols.) with subsequent acidification, separates from dilute alcohol in large, colourless, acicular crystals which melt at 163—163·5°, and when heated rapidly, volatilise unchanged; it is very soluble in pyridine,

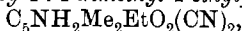
less so in alcohol or boiling water, and very slightly in ether. Its aqueous solution has a marked acid reaction, and when neutralised with ammonia gives a voluminous white precipitate with silver nitrate solution. It contains two hydrogen atoms replaceable by silver; the *mono-silver*, $C_{10}H_{10}O_2N_3Ag$ [$Ag = 2$ or 3], and the *di-silver*, $C_{10}H_8O_2N_3Ag_2$ [$Ag : Ag = 3 : 5$ or $2 : 6$], derivatives are both white precipitates. The *dibromo*-derivative separates from dilute acetic acid solution in colourless laminæ or short prisms which melt at $144-145^\circ$, and decompose at about 200° with evolution of bromine. On heating the dibromo-compound with excess of 50 per cent. acetic acid, it yields

3 : 5-Dicyano-1 : 4 : 4-trimethyltrimethylenedicarbonimide,



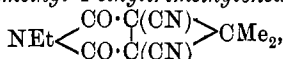
which separates from alcohol in acicular crystals melting at 241.5° , and dissolves readily in pyridine, less so in alcohol, and to a slight extent in water; it sublimes in the form of a bulky mass of slender needles, gives a neutral aqueous solution, not precipitated by silver nitrate in presence of ammonia, and does not absorb bromine.

3 : 5-Dicyano-2 : 6-dioxy-4 : 4-dimethyl-1-ethylpiperidine,



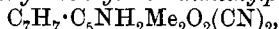
obtained by the interaction of acetone, ethyl cyanoacetate and alcoholic ethylamine, separates from dilute alcohol in hard, sparkling, colourless crystals melting at $110.5-111.5^\circ$; it is very soluble in pyridine or alkali solutions, less so in alcohol, and only to a slight extent in water, giving an acid solution. Its *dibromo*-derivative separates from dilute acetic acid in colourless, prismatic crystals which melt at $130-132^\circ$ and are soluble in acetic acid. Heated with 50 per cent. acetic acid, the dibromo-compound is converted into

3 : 5-Dicyano-4 : 4-dimethyl-1-ethyltrimethylenedicarbonimide,



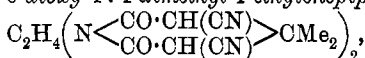
which separates in hard, heavy crystals melting at 211° and subliming in very light, colourless needles; it is very soluble in pyridine, slightly so in water, and has a neutral reaction.

3 : 5-Dicyano-2 : 6-dioxy-1-benzyl-4 : 4-dimethylpiperidine,



prepared from acetone, ethyl cyanoacetate, and alcoholic benzylamine, separates from dilute alcohol in long, silky needles which melt at $149-150^\circ$ and dissolve in potassium hydroxide solution. It has an acid reaction and when neutralised with sodium hydroxide solution behaves like a monobasic acid.

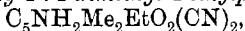
3 : 5-Dicyano-2 : 6-dioxy-4 : 4-dimethyl-1-ethylenepiperidine,



obtained from acetone, ethyl cyanoacetate, and alcoholic ethylenediamine, crystallises from dilute alcohol in small plates which become yellow at 250° and melt and decompose at $287-290^\circ$; it dissolves slightly in alcohol, and to a less extent in water, yielding an acid solution; it behaves as a dibasic acid towards sodium hydroxide, and gives a white, insoluble, *silver* salt and coloured, insoluble *copper* and *ferrous* derivatives.

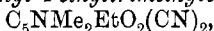
3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-ethylpiperidine, when neutralised with ammonia or sodium hydroxide, gives off a little ethane (see Grande, Abstr., 1898, i, 272); if magnesium hydroxide is used for the neutralisation, the amount of ethane obtained corresponds with the resolution of the piperidine derivative into dicyano- γ -methylglutaconimide and ethane.

3 : 5-Dicyano-2 : 6-dioxy-1 : 4-dimethyl-4-ethylpiperidine,



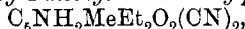
obtained from methyl ethyl ketone, ethyl cyanoacetate, and alcoholic methylamine, separates from dilute alcohol in sparkling laminae or small crystals melting at 192.5° ; it dissolves readily in pyridine, less so in alcohol or acetic acid, and slightly in water, forming an acid solution which, with ammonia and silver nitrate, yields a white precipitate; the aqueous solution gives a white precipitate with chlorine or bromine water, and when neutralised with ammonia decomposes into ethane and an unstable ammonium derivative of dicyano-1 : 4-dimethylglutaconimide which is immediately resolved into ammonia and dicyano-1 : 4-dimethylglutaconimide. The dibromo-derivative, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3\text{Br}_2$, separates from dilute acetic acid in hard, prismatic, colourless crystals melting at $106-107.5^\circ$ and when heated with acetic acid yields

3 : 5-Dicyano-1 : 4-dimethyl-4-ethyltrimethylenedicarbonimide,



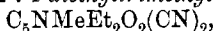
which crystallises from dilute alcohol in colourless needles melting at $161-162^\circ$ and subliming in the form of very slender needles; it is soluble in alcohol or acetic acid and slightly so in water, giving a neutral solution, and it does not combine with bromine.

3 : 5-Dicyano-2 : 6-dioxy-4-methyl-1 : 4-diethylpiperidine,



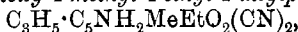
prepared by the interaction of methyl ethyl ketone, ethyl cyanoacetate, and alcoholic ethylamine, crystallises from dilute alcohol in colourless laminae which melt at $146-147.5^\circ$ and dissolve slightly in water, giving an acid solution; on neutralising the latter with ammonia, ethane is evolved. The dibromo-derivative separates from dilute acetic acid in colourless crystals melting at $112-115^\circ$, and when heated with 50 per cent. acetic acid yields

3 : 5-Dicyano-4-methyl-1 : 4-diethyltrimethylenedicarbonimide,



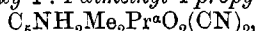
which crystallises from dilute acetic acid in light needles melting at 155.5° ; it is soluble in pyridine or alcohol.

3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-ethyl-1-allylpiperidine,



prepared from methyl ethyl ketone, ethyl cyanoacetate, and alcoholic allylamine, crystallises from dilute alcohol in long, sparkling needles which melt at $91-92^\circ$ and dissolve slightly in water, giving an acid solution.

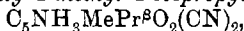
3 : 5-Dicyano-2 : 6-dioxy-1 : 4-dimethyl-4-propylpiperidine,



obtained from methyl propyl ketone, ethyl cyanoacetate, and alcoholic methylamine, crystallises from water in sparkling laminae which melt at $134-135.5^\circ$ and dissolve in alcohol, and to a less extent in water,

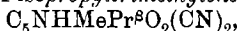
yielding a strongly acid solution; it is soluble in alkali solution, and in presence of ammonia and mercury decomposes with evolution of propane.

3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-isopropylpiperidine,



prepared from methyl isopropyl ketone, ethyl cyanoacetate, and ammonia, crystallises in plates melting at $232-234^\circ$; when neutralised with ammonia, propane is evolved. The dibromo-derivative, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3\text{Br}_2$, melts at $163-165^\circ$.

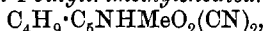
3 : 5-Dicyano-4-methyl-4-isopropyltrimethylenedicarbonimide,



has an acid reaction, and crystallises in prisms melting at about 240° .

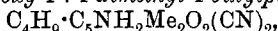
[With CARLO MENSIO.—3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-butylpiperidine, $\text{C}_4\text{H}_9\cdot\text{C}_5\text{NH}_3\text{MeO}_2(\text{CN})_2$, prepared from methyl butyl ketone, ethyl cyanoacetate, and alcoholic ammonia, separates from water in broad, nacreous plates which melt at $180-182^\circ$ and dissolve readily in acetone, pyridine, or alkali solutions; on treating the aqueous solution with ammonia or magnesium hydroxide, butane is evolved. The silver salt, $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_3\text{Ag}$, was prepared, and the dibromo-derivative, $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_3\text{Br}_2$, which forms colourless crystals melting at $128-129^\circ$ and is soluble in acetic acid. When heated with 50 per cent. acetic acid, the dibromo-compound yields

3 : 5-Dicyano-4-methyl-4-butyltrimethylenedicarbonimide,



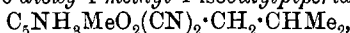
which forms white plates soluble in water and melting at $188-189^\circ$; when heated with dilute sodium hydroxide solution, it yields ammonia and the sodium salt of methylbutyldicyanotrimethylenedicarboxylic acid; the silver salt of the imide was prepared.

3 : 5-Dicyano-2 : 6-dioxy-1 : 4-dimethyl-4-butylpiperidine,



prepared from methyl butyl ketone, ethyl cyanoacetate, and alcoholic methylamine, crystallises from dilute alcohol in colourless prisms melting at 123° and, when neutralised with ammonia, yields butane.

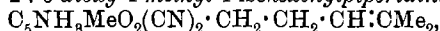
3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-isobutylpiperidine,



crystallises from dilute alcohol in long needles melting at $241-242^\circ$ and is soluble in alkaline hydroxide or carbonate solution, or in alcohol, and to a slight extent in water, giving an acid solution; it decolorises bromine, and when neutralised with ammonia or magnesium hydroxide yields butane.

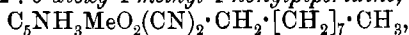
[With SILVIO BALDI.—3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-isohexylpiperidine, $\text{C}_5\text{NH}_3\text{MeO}_2(\text{CN})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}_2$, prepared from methyl isohexyl ketone, ethyl cyanoacetate, and alcoholic ammonia, crystallises from alcohol in sparkling laminæ melting at $166.5-168.5^\circ$; it is almost insoluble in water, has an acid reaction, and forms a dibromo-derivative.]

3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-isohexenylpiperidine,



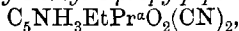
prepared from methyl heptenone, ethyl cyanoacetate, and alcoholic ammonia, crystallises from alcohol in shining laminæ melting at $183-184.5^\circ$; it is soluble in alcohol, acetone, pyridine, or acetic acid, and slightly so in water, giving an acid solution.

3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-nonylpiperidine,



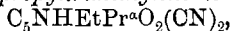
crystallises from alcohol in nacreous plates which melt at 136.5 — 137.5° and are greasy to the touch ; it is soluble in alcohol or acetic acid and in potassium hydroxide or ammonia solution. The ammonium salt decomposes with evolution of nonane ; the *silver*, *copper*, *calcium*, and *barium* salts and the *dibromo*-derivative were prepared.

3 : 5-Dicyano-2 : 6-dioxy-4 ethyl-4 propylpiperidine,



crystallises from dilute alcohol in sparkling plates melting at 216 — 217° ; it is very soluble in pyridine and slightly so in water, yielding an acid solution which gives a white precipitate with aqueous chlorine or bromine ; with potassium permanganate, it yields hydrogen cyanide, and the aqueous solution neutralised with ammonia does not evolve propane but ethane, the corresponding ammonium derivative of propyldicyanoglutaconimide being also formed ; the *silver* and *cuprammonium* salts of this latter compound were also prepared. The *dibromo* derivative of the dioxypiperidine, $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_3\text{Br}_2$, separates from dilute acetic acid in colourless prisms melting at 159 — 161° , and when heated with acetic acid is converted into

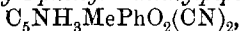
3 : 5-Dicyano-4-ethyl-4-propyltrimethylenedicarbonimide,



crystallising in sparkling needles which melt at 186 — 186.5° and are soluble in alcohol.

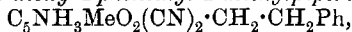
3 : 5-Dicyano-2 : 6-dioxy-4 : 4-dipropylpiperidine, $\text{C}_5\text{NH}_3\text{Pr}^a_2\text{O}_2(\text{CN})_2$, prepared from dipropyl ketone, ethyl cyanoacetate and alcoholic ammonia, separates from dilute alcohol either in long, silky needles or in heavy, prismatic crystals melting at 220.5° ; it dissolves very readily in pyridine, less so in dilute potassium hydroxide or ammonia solution ; in aqueous solution, it is decomposed by magnesium hydroxide and very rapidly by ammonia solution with evolution of propane, whilst calcium hydroxide is without action. Its *dibromo* derivative separates from dilute acetic acid in dense, rhombic plates which melt at 136 — 138° and are soluble in acetic acid.

3 : 5-Dicyano-2 : 6-dioxy-4-phenyl-4-methylpiperidine,



prepared from acetophenone, ethyl cyanoacetate, and alcoholic ammonia, separates from alcohol in nacreous laminae which become brown at about 270° and melt at about 280° ; it dissolves slightly in water and on neutralisation with alkalis behaves as a monobasic acid.

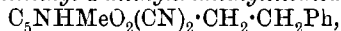
3 : 5-Dicyano-2 : 6-dioxy-4-phenethyl-4-methylpiperidine,



crystallises from alcohol in shining, colourless, rhombic plates with blunted angles and melts at 223 — 224.5° to a reddish-brown liquid ; when partially neutralised with dilute ammonia solution, it gradually decomposes into ethylbenzene and the ammonium salt of dicyanomethylglutaconimide ; towards alkalis, it behaves like a dibasic acid. It forms white, crystalline *ammonium* and *magnesium* salts, a yellow, insoluble *copper* salt, and a white, sparingly soluble *silver* salt. The *dibromo*-derivative, $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}_3\text{Br}_2$, separates from dilute acetic acid

in blunt-angled, shining rhombs melting at 163—165°, and when heated with 50 per cent. acetic acid yields

3 : 5-Dicyano-4-phenethyl-4-methyltrimethylenedicarbonimide,



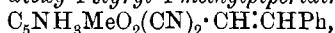
which separates from dilute acetic acid in dense, colourless crystals melting at 203—205°; it dissolves sparingly in water, giving an acid solution, and when mixed with dilute sodium hydroxide solution and distilled in a current of steam it yields ammonia and 1 : 2-dicyano-3-methyl-3-phenethyltrimethylene-1 : 2-dicarboxylic acid.

3 : 5-Dicyano-2 : 6-dioxy-4-phenethyl-1 : 4-dimethylpiperidine,



crystallises from alcohol in needles melting at 203—204°; it is slightly soluble in water, more so in acetic acid or alkali solution, and behaves as a monobasic acid.

3 : 5-Dicyano-2 : 6-dioxy-4-styryl-4-methylpiperidine,



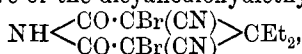
obtained from benzylideneacetone, ethyl cyanoacetate, and alcoholic ammonia, melts at 275—277°, and on treating with ammonia and acidifying with hydrochloric acid, yields a compound separating in the form of short prisms or rhombic plates, melting and decomposing with evolution of gas at 281—283°; this compound is being further investigated.

From the results obtained in the preparation of the compounds above described, the following conclusions are drawn. Ketones containing normal chains react most readily with ethyl cyanoacetate and ammonia, or an amine, to form dicyanodioxypiperidine derivatives. The prolongation of one of the normal alkyl groups of the ketone increases the amount of product obtained, a result which is also produced by the presence of phenyl in one of the alkyl radicles. When the two radicles of the ketone are identical, the amount of product obtained decreases as the radicle increases in size. *iso* Ketones containing a CH_2 group, give good results, but with those in which a secondary, or tertiary, carbon atom is united directly with the carbonyl group, the reaction takes place with difficulty. With aromatic ketones having a phenyl radicle in direct combination with the carbonyl group, the reaction proceeds either with difficulty or not at all, but the opposite is the case if one or more CH_2 groups intervene between the phenyl and carbonyl radicles. In the decomposition of the ammonium or magnesium compounds of the dicyanodioxypiperidine derivatives prepared from ketones of the form $\text{CH}_3 \cdot \text{CO} \cdot \text{R}$, methane is never evolved, but always a hydrocarbon of higher molecular weight. Other theoretical considerations, such as the influence of the large number of electro-negative groups present in the molecules of these compounds on their acid character, are discussed. The author is continuing his researches.

T. H. P.

Derivatives of Diethyl Ketone. By EDOARDO PEANO (*Atti Accad. Sci. Torino*, 1900—1901, 36, 187—195).—3 : 5-Dicyano-2 : 6-dioxy-4 : 4-diethylpiperidine, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CH}(\text{CN}) \\ \text{CO} \cdot \text{CH}(\text{CN}) \end{smallmatrix} > \text{C}_2\text{H}_5$, obtained together with cyanacetamide by the interaction of diethyl ketone, ethyl

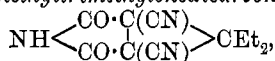
cynoacetate, and alcoholic ammonia, forms thin, colourless, shining leaflets which melt at 200° , and dissolve slightly in water and to a greater extent in alcohol. The *silver* salt, $C_{11}H_{12}O_2N_3Ag$, is a white precipitate, and the *cuprammonium* salt, $(C_{11}H_{12}O_2N_3)_2Cu \cdot 4NH_3 \cdot H_2O$, forms bluish-violet crystals. On neutralising the aqueous solution with ammonia or magnesium hydroxide, it decomposes into ethane, and the ammonium salt of 3:5-dicyano-4-ethylglutaconimide already obtained by Treves (*Atti Accad. Sci. Torino*, 1899, 34) by the action of ethyl cyanoacetate on propaldehyde in presence of ammonia. The *dibromo*-derivative of the dicyanodioxidiethylpiperidine,



crystallises from dilute acetic acid in short prisms, melting and decomposing at 182° .

By distillation with sodium hydroxide solution, the piperidine compound is decomposed into ammonia and sodium 1:2 dicyano-3:3-diethyltrimethylene-1:2-dicarboxylate.

3:5-Dicyano-4:4-diethyltrimethylenedicarbonimide,



obtained by the action of acetic acid on the dibromo-compound above described, melts at 202° and forms a *silver* salt obtained as a white precipitate. T. H. P.

Action of Nitric Acid on Tetriodopyrrole (Iodole). By H. COUSIN (*J. Pharm.*, 1901, [vi], 13, 269—272).—When tetriodopyrrole in ethereal solution is treated in the cold with a mixture of nitric and acetic acids, it yields two nitro-compounds, of which the more abundant *nitrotriiodopyrrole*, $C_4NHl_3 \cdot NO_2$, crystallising in stellate groups of golden-yellow, prismatic needles, can be separated from the second by its much greater solubility in absolute alcohol. It is very sparingly soluble in hot water, benzene, or chloroform, but copiously in ether, and decomposes at 185 — 187° without fusion; the hydrogen atom is replaceable by metals, with formation of reddish-orange, explosive salts. The second compound is reserved for future investigation.

Dinitrodiiodopyrrole, $C_4NHl_2(NO_2)_2$, formed by the action of fuming nitric acid at 100° on the preceding compound, forms golden-yellow, crystalline plates, sparingly soluble in cold water, readily so in alcohol, melts and decomposes at 190 — 192° , and forms reddish-orange alkali salts, that of potassium being sparingly soluble in cold water.

M. J. S.

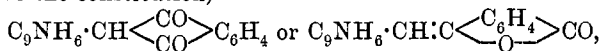
Studies on Isatin. By LEON MARCHLEWSKI and J. BURACZEWSKI (*Bull. Acad. Sci. Cracow*, 1900, 374—376. Compare *Abstr.*, 1900, i, 100).—The condensation of acetyl- ψ -isatin with *o*-phenylenediamine produces *o*-aminophenylhydroxyquinoxaline, and not *o*-aminophen-imesatine (*loc. cit.*). For both indophenazine and a quinoxaline derivative to be formed from isatin and *o*-phenylenediamine in aqueous solution, the isatin must either be present as isatinic acid or as a mixture of lactim and lactam.

o-Acetylaminophenylhydroxyquinoxaline, *o*-nitrophenylhydroxyethoxy-

quinoxaline, and *o*-acetylaminophenylhydroxymethylquinoxaline, have been prepared.

The products of alkylation of indophenazine are identical with the condensation products of alkyl- ψ isatins with *o*-phenylenediamine, but the condensation of alkylated *o*-diamines with isatin leads to the formation of isomerides of the alkyl-indophenazines; these are called by the author alkyl- ψ -indophenazines. Of the indophenazine series, a *carboxylic acid*, and two isomeric *ethoxyindophenazines* have been prepared. Methyl- ψ -isatin and semicarbazide react, yielding two isomerides of the formula $C_{10}H_{10}O_2N_4$. K. J. P. O.

Constitution of Quinophthalone and the Two Isomeric Quinophthalones. By ALEXANDER EIBNER and O. LANGE (*Annalen*, 1901, 315, 303—356).—Quinophthalone, the base of quinoline-yellow, is produced by condensing quinaldine with phthalic anhydride; it may have the constitution,



according as to which oxygen atom of the anhydride is eliminated in the condensation. The experimental results now obtained support the view that the colouring matter possesses the asymmetric constitution represented by the second of these formulæ.

On adding bromine to an acetic acid solution of quinophthalone, a mixture of bromo-derivatives is obtained. The *tribromo*-compound, $C_{18}H_{10}O_2NBr_3$, is precipitated from the acetic acid solution in orange-red needles which become yellow at 200° and melt at 228° ; this substance when shaken with water yields the original base, and when treated with absolute alcohol gives rise to the *monobromo*-compound, $C_{18}H_{10}O_2NBr$, which is also produced by direct bromination; it crystallises in yellow needles, melts at 174° , and when boiled with alcohol or warmed for a short time with solutions of the alkali hydroxides or carbonates is reconverted into quinophthalone.

Dinitroquinophthalone, $C_{18}H_{11}O_6N_3$, produced by passing nitrogen tetroxide into a cooled glacial acetic acid solution of quinophthalone, is precipitated, on the addition of water, in white flakes; it melts indefinitely at about 133° . *Nitroquinophthalone*, $C_{18}H_{10}O_4N_2$, obtained by the action of the nitrous fumes from nitric acid and arsenious oxide on quinophthalone dissolved in acetic acid, crystallises in felted, yellow needles, and melts at 140° . It is also produced by boiling the preceding compound with alcohol, and is itself reconverted into the original colouring matter by the action of alkalis or dilute acids.

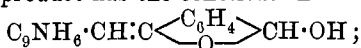
The ease with which quinophthalone is regenerated from its bromo- and nitro-derivatives indicates that the substances are of the nature of additive products, the formation of which depends on the existence, in its molecule, of a double linking corresponding with that indicated in the asymmetric formula. Phthalic chloride, which is represented as having an asymmetric constitution, condenses with quinaldine to

form a compound, $C_9NH_8 \cdot CH_2 \cdot C(OH) \begin{array}{c} \diagup C_6H_4 \\ \diagdown O \end{array} CO$, which crystallises in yellow needles, melts at 124° , and when heated, either alone or with sodium hydroxide solution, yields quinophthalone. This condensation

product is also obtained as an intermediate step in the preparation of quinophthalone, providing that the temperature is maintained below 150° .

An almost quantitative yield of quinophthalone is obtained by heating on the water-bath a mixture of diethyl phthalate, quinaldine, and sodium wire; it is also readily produced by adding bromine to a benzene solution of phthalidylquinaldine (m. p. 104°), and heating the *dibromide*, $C_{18}H_{12}O_2NBr_2$, until the evolution of hydrogen bromide ceases. Nencki (Abstr., 1896, i, 256) assigned to phthalidylquinaldine the constitution $C_9NH_6 \cdot CH_2 \cdot CH \langle \underset{O}{\overset{C_6H_4}{\rangle}} CO$, supposing that the hydroxyl group of

phthalaldehydic acid, $OH \cdot CH \langle \underset{O}{\overset{C_6H_4}{\rangle}} CO$, had been eliminated in the condensation; the preceding results are, however, more readily explained on the assumption that the carbonyl group is involved in the condensation, and that the product has the constitution



this substance could take up 2 atoms of bromine to form a dibromide, $C_9NH_6 \cdot CHBr \cdot CBr \langle \underset{O}{\overset{C_6H_4}{\rangle}} CH : OH$, from which quinophthalone would be obtained by the subsequent elimination of hydrogen bromide. The dibromide is quite stable in boiling benzene, and crystallises from this solvent in colourless leaflets melting at 108° .

Quinophthalone forms unstable alkali derivatives when treated with alcoholic solutions of the alkali hydroxides, but is not decomposed on heating at 200° with excess of sodium methoxide or the corresponding ethyl or amyl derivative.

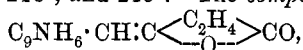
Quinophthaloneanil, $C_9NH_6 \cdot CH : C \langle \underset{O}{\overset{C_6H_4}{\rangle}} C : NPh$, produced by heating together a mixture of aniline, zinc chloride, and the colouring matter, crystallises from alcohol or chloroform in red, felted needles and melts at 232° ; it is also readily obtained by condensing its generators in a benzene solution in the presence of aluminium chloride. The anil is hydrolysed either by acid or alkalis. α -Quinophthaline, $C_9NH_6 \cdot CH : C \langle \underset{O}{\overset{C_6H_4}{\rangle}} C : NH$, produced by heating quinophthalone with alcoholic ammonia at 200° , melts at 305° , and yields a *platini-chloride* and a *bromo-derivative*, $C_{18}H_{11}ON_2Br$, melting respectively at 278° and 100° ; it is readily decomposed by aniline or phenylhydrazine, the former base giving rise to quinophthaloneanil whilst the latter furnishes a *compound*, $C_{24}H_{17}ON_3$, crystallising in red, felted needles and melting at 165° . α -Quinophthaline is readily hydrolysed to quinophthalone by mineral acids and also when heated to 200° with methyl alcohol. These reactions indicate that the base is an imino-derivative of quinophthalone, the imino-group being, in fact, eliminated in the form of ammonia in the foregoing decompositions.

An isomeric base, β -quinophthaline, $C_9NH_6 \cdot CH : C \langle \underset{NH}{\overset{C_6H_4}{\rangle}} CO$, produced by slowly adding phthalimide to a mixture of quinaldine and zinc chloride heated at $160-180^{\circ}$, separates in the form of its *sulphate*,
 $C_{18}H_{12}ON_2, H_2SO_4$.

on dissolving the fused mass in concentrated sulphuric acid and pouring the solution into water. The base separates from acetic acid or alcohol in yellow, cubic crystals and melts at 213° ; it is less basic than its isomeride and dissolves more readily in the organic solvents. Its salts are yellow and amorphous, it forms a *silver* derivative, $C_{18}H_{11}ON_2Ag$, but does not interact with the alkali hydroxides, phenylhydrazine, acetic anhydride or benzoic chloride. Unlike its α -isomeride, it is not easily converted into quinophthalone on heating with mineral acids, the action only taking place in sealed tubes at temperatures above 100° . The base, when treated with bromine in glacial acetic acid solution, yields a mixture of *mono*- and *tri*-bromo-derivatives melting respectively at 56 — 59° and 170° ; the monobromo-compound, when boiled with alcohol or warmed with alkaline solutions, is reconverted into the original substance.

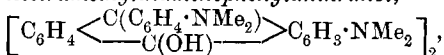
β -Quinophthaline and aniline do not react even at boiling point of the latter base, but on adding zinc chloride to the mixture ammonia is eliminated, and quinaldine and phthalanil are produced.

Succinimidequinaldine, $C_9NH_6 \cdot CH:C \left\langle \begin{smallmatrix} C_2H_4 \\ NH \end{smallmatrix} \right\rangle CO$, prepared by heating together succinimide, quinaldine, and zinc chloride, dissolving the product in concentrated sulphuric acid, adding the solution to water, and decomposing the precipitated sulphate by ammonia, crystallises from alcohol in feathery aggregates of leaflets and melts at 128° ; it sublimes at higher temperatures and decomposes at 220° . Its solution in neutral solvents exhibits an intense green fluorescence which is diminished by the addition of acids; the substance separates from benzene in thick, lemon-yellow crystals having a violet reflex. The *hydrochloride* crystallises in yellow needles, the sulphate and the *platinichloride*, $C_{14}H_{12}ON_2 \cdot H_2PtCl_6$, in yellow prisms, these salts melt respectively at 240° , 218° , and 215° . The compound



analogous to quinophthalone, could not be obtained by the direct condensation of quinaldine and succinic anhydride; it was, however, prepared by heating the preceding base with hydrochloric acid at 100° . The product crystallises from alcohol in aggregates of brilliant yellow needles, and melts at 108° . G. T. M.

Tetramethyldiaminophenylantranol and Tetramethyldiaminophenylloxantranol. By ALBIN HALLER and ALFRED GUYOT (*Bull. Soc. Chim.*, 1901, [iii], 25, 315—322).—Dimethylaminobenzoylbenzoic acid condenses with dimethylaniline in the presence of acetic anhydride to form dimethylanilinophthalein, $CO \left\langle \begin{smallmatrix} O \\ C_6H_4 \end{smallmatrix} \right\rangle C(C_6H_4 \cdot NMe_2)_2$, which is reduced by zinc in hydrochloric acid solution to dimethylanilinophthalin or tetramethyldiaminotriphenylmethane-*o*-carboxylic acid, $CO_2H \cdot C_6H_4 \cdot CH(C_6H_4 \cdot NMe_2)_2$. The latter compound, when dissolved in dimethylaniline and treated with phosphorus oxychloride, condenses to *bistetramethyldiaminophenylantranol*,



which crystallises from boiling toluene in large scales containing 1 mol. of the solvent; when heated to 200° , it becomes phosphorescent through oxidation, and melts at about 275° . *Tetramethyldiaminophenylloxanthranol*, $\text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2) \cdot \text{OH}$, obtained by oxidising $\text{CO}-\text{C}_6\text{H}_3 \cdot \text{NMe}_2$

the preceding compound with potassium dichromate or ferric chloride, crystallises from chloroform in large, pale-yellow prisms melting at 213° , dissolves in sulphuric acid with the red coloration characteristic of phenylloxanthranols, and differs entirely from the substance described under the same name by O. Fischer (*Annalen*, 1881, 206, 112). In the oxidation of the anthranol, a fugitive blue coloration is observed, which is due to the formation of an unstable *salt*, which subsequently undergoes hydrolysis; it forms, with zinc chloride, a rather more stable *compound*, crystallising in small, bronze coloured needles.

N. L.

The Law of Auxochromes. By PAUL LEMOULT (*Compt. rend.*, 1901, 132, 784—787).—The author contends, in reply to Camichel and Bayrac (this vol., i, 296) that the law of auxochromes holds good for triphenylmethane derivatives containing 2 atoms of tertiary nitrogen, as in tetramethyldiaminotriphenylcarbinol oxalate and tetraethyldiaminotriphenylcarbinol sulphate, or 3 atoms of tertiary nitrogen as in hexaethyltriaminotriphenylcarbinol hydrochloride, and sodium dimethyldiethyldibenzyltriaminotriphenylcarbinoldisulphonate. Diagrams of the spectra are given, showing that the maximum of the unabsorbed red band is the same for both members of each of these pairs of compounds, but differs in the case of the two pairs. Care is required to determine the exact position of maximum transparency and the selection of a suitable degree of dilution of the solution is important.

C. H. B.

Action of Aniline and of Ammonia on 5-Chloro-1-phenyl-3-methylpyrazole Methochloride. By AUGUST MICHAELIS and E. GUNKEL (*Ber.*, 1901, 34, 723—727).—The compound formed by heating aniline with antipyrine and phosphorus oxychloride (Silberstein, German Patent, 1899, 113384) probably owes its origin to the intermediate formation of 5-chloro-1-phenyl-3-methylpyrazole methochloride (*Abstr.*, 1899, i, 941), as it is obtained when the latter is heated with aniline for 8 hours at 250° ; it probably therefore is an

aniloantipyrine (anilopyrine) of the formula, $\begin{array}{c} \text{CMe}=\text{NMe} \\ | \\ \text{NPh} < \text{C} \text{---} \text{NPh} \\ | \\ \text{CH}=\text{C} \end{array}$, cor-

responding with the formula $\begin{array}{c} \text{CMe}=\text{NMe} \\ | \\ \text{O} < \text{C} \text{---} \text{NPh} \\ | \\ \text{CH}=\text{C} \end{array}$ for antipyrine. This

constitution is more probable than $\begin{array}{c} \text{CMe}-\text{NMe} \\ | \\ \text{CH} \cdot \text{C}(\text{NPh}) \end{array} > \text{NPh}$, as the substance is not changed when heated with hydrochloric acid at 150° or with alcoholic potassium hydroxide, whereas benzylideneaniline, $\text{CHPh}:\text{NPh}$, and similar compounds always lose aniline when similarly treated.

With excess of nitric acid, anilopyrine yields two *compounds*, one

almost insoluble in alcohol, and the *other* easily soluble. The former crystallises from glacial acetic acid in red needles, and has the composition $C_{12}H_8N_3 \cdot NO_2$, as it yields on reduction with tin and hydrochloric acid an *amino*-compound, $C_{12}H_8N_3 \cdot NH_2$, which crystallises from alcohol in small, dark-red, lustrous leaflets and melts at 215° ; the latter forms citron-yellow leaflets, melts at 164° , and probably also contains a nitro-group.

Anilopyrine combines with methyl iodide at 100° to form the compound, $C_{17}H_{17}N_3 \cdot MeI$, which crystallises from water in yellowish prisms and melts at 174° .

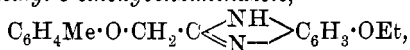
Aqueous or alcoholic ammonia does not act on antipyrine chloride (5-chloro-1-phenyl-3-methylpyrazole methochloride) at a high temperature, but ammonium carbonate after 12 hours at 200° yields *iminopyrine*, $C_{11}H_{12}N_2 \cdot NH$, which crystallises from toluene in white needles and melts at 116° .
W. A. D.

Acetylenic Ketones. Synthesis of β -Diketones. By CHARLES MOUREU and RAYMOND DELANGE (*Bull. Soc. Chim.*, 1901, [iii], 25, 302—313).—Mainly an account of work already published (*Abstr.*, 1900, i, 397; this vol., i, 14. Compare also Nef, *Abstr.*, 1900, i, 20). The action of semicarbazide on benzoylheptinene results in the formation of hydrazodicarbonamide and 3-phenyl-5-amyldipyrzole, which crystallises from light petroleum in slightly yellow prisms melting at 76° . This substance is also produced by the action of hydrazine sulphate on benzoylheptinene.
N. L.

Aromatic Phenoxyacetamidines. By GEORG COHN (*J. pr. Chem.*, 1901, [i], 63, 188—192).—By the condensation of phenoxyacetic acid and some of its derivatives with the *o*-diamines, 3:4-diaminophenetole or 3:4-tolylenediamine, the following phenoxyacetamidines have been obtained, the condensation being brought about by heating mixtures of the acid and base at about 150° .

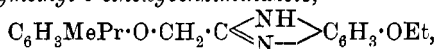
2-Phenoxyethyl-6-ethoxybenzimidazole, $OPh \cdot CH_2 \cdot C \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} > C_6H_3 \cdot OEt$, forms colourless plates melting at 168 — 169° ; the *hydrochloride* melts at 205° , and the *picrate*, which forms thin plates, at 211 — 212° .

2-p-Tolyloxyethyl-5-ethoxybenzimidazole,



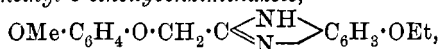
crystallises in colourless plates melting at 145 — 146° ; the *picrate* forms a crystalline precipitate melting at 226 — 227° .

2-m-Thymoxyethyl-5-ethoxybenzimidazole,



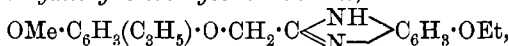
melts at 84 — 86° ; the *hydrochloride* forms plates from alcohol melting at 208° ; the *picrate* melts at 194° . The isomeric *carvacrol* derivative melts at 124 — 125° ; the *picrate* crystallises in greenish-yellow plates melting at 204° .

2-Guaiacoxymethyl-5-ethoxybenzimidazole,



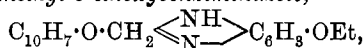
crystallises in faintly violet needles melting at 122—123°; the *picrate* forms large, greenish needles which melt at 174°.

2-m-Eugenoxymethyl-5-ethoxybenziminazole,



forms needles melting at 75—76°; the *hydrochloride* forms greenish needles, and the *picrate* needles melting at 125°.

2- α -Naphthylloxymethyl-5-ethoxybenziminazole,

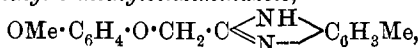


melts at 190°, and forms a *picrate* melting at 227—228°. The β -naphthyl derivative melts at 163—165°, the *hydrochloride* at 221°, and the *picrate* at 249—250°, both decomposing.

2-Phenoxymethyl-5-methylbenziminazole, $\text{OPh} \cdot \text{CH}_2 \cdot \text{C} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}_6\text{H}_3\text{Me}$,

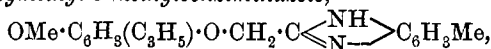
melts at 170—171°; the *picrate* forms yellow needles melting at 216—217°.

2-Guaiacoxymethyl-5-methylbenziminazole,



forms star-shaped aggregates of needles melting at 78—80°; the *picrate* melts at 179°.

2-Eugenoxymethyl-5-methylbenziminazole,



forms lustrous plates melting at 71—73°; the *picrate* melts at 132°.

K. J. P. O.

Condensation of Glyoxal and Benzaldehyde with Ammonia.

By L. WEWIÓRSKI (*Bull. Acad. Sci. Cracow*, 1900, 398—399).—By the action of ammonia on a dilute aqueous solution of glyoxal and benzaldehyde, a 60 per cent. yield of 2-phenylglyoxaline is obtained. When ammonia gas is employed, and alcohol used as the solvent, hydrobenzamide, glyoxaline, glycosine, and much tarry substance are formed.

2-Phenylglyoxaline crystallises in white scales or needles melting at 148°; the *hydrochloride* forms long, white needles melting at 67·5—68°; the *sulphate* melts at 186—187°; the *platinichloride* forms orange-yellow needles. 2-Phenyl-1-methylglyoxaline and 2-phenyl-1-ethylglyoxaline are oily liquids; the latter boils at 300—305°, and has a sp. gr. 1·0522 at 18°, and a molecular refraction 54·49.

K. J. P. O.

Chemistry of Elastic Ligament. By A. N. RICHARDS and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1900, xi—xii; *Amer. J. Physiol.*, 5).—Ligamentum nuchæ of the ox contains appreciable quantities of mucin, having all the characters of the glucoproteid separable from white fibrous tissue. Like coagulable proteids, it is easily removed by extraction for a few days with lime water. This renders subsequent extraction with hot alkali unnecessary. Elastin prepared after such extraction contains less sulphur (0·13 to 0·17 per

cent.) than that prepared by older methods. The distribution of nitrogen by Schultze's method is 1.73 as ammonia, 3.08 as bases, and 95.23 as amino-acids.

W. D. H.

Chemical Nature of the Tetanus Poison, and the Chemistry of Albumoses. By H. HAYASHI (*Chem. Centr.*, 1901, i, 411—412; from *Comm. Med. Fac. Imp. Jap. Univ., Tokio*, 4, 341—362).—The precipitate formed by adding zinc chloride to a solution of Witte's peptone which has been treated with sodium carbonate solution is a double compound of basic zinc carbonate and albumoses, and contains at the most only traces of peptones. This "zinc carbonalbumosate" in the moist state is soluble in ammonium sulphate solution and the albumoses are precipitated from the solution by saturating it with ammonium sulphate. The zinc compound of the tetanus poison (compare Brieger and Fraenkel, *Ber. klin. Woch.*, 27, 241) is soluble in sodium hydroxide solution, and gives the biuret reaction (compare Brieger and Boer, *Zeit. Hyg.*, 21, 259). The poisonous compound obtained from this substance, however, contains zinc. From the behaviour of the zinc compound, the author concludes that the tetanus poison may belong to the group of albumoses, or that it contains an albumose combined with the poisonous substance, or that the latter is only carried down mechanically. The zinc compound is decomposed by ammonium sulphate and contains peptones in a state of combination. When the tetanus culture is neutralised with magnesium carbonate instead of with sodium carbonate, zinc chloride does not precipitate the whole of the poison.

E. W. W.

Antipeptone By FR. KUTSCHER (*Ber.*, 1901, 34, 504—506).—A reply to Siegfried (this vol., i, 176).

C. F. B.

Epinephrine. By JOHN J. ABEL (*Proc. Amer. Physiol. Soc.*, 1900, v—vi. Compare *Abstr.*, 1899, i, 395; 1900, i, 72).—If the autoclave is not used in the preparation of epinephrine, a more active product is obtained. Von Fürth's suprarenine (*Abstr.*, 1900, ii, 292) is only a modification of epinephrine, being the native principle not subjected to benzoating or treatment in the autoclave.

W. D. H.

Nature of Melanins and Allied Substances. By V. DUCCESCHI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 180—188).—By the action of concentrated hydrochloric acid and potassium chlorate on tyrosine, a compound is obtained giving reactions identical with those of melanoidic acid prepared by Schmiedeberg by treating serum albumin with dilute hydrochloric acid (*Abstr.*, 1898, i, 342).

When tyrosine is treated with concentrated hydrochloric acid and sodium nitrite, it yields a substance having all the reactions and properties given by von Fürth ("The Action of Nitric Acid on Proteids," Strassburg, 1899) as characteristic of the xanthomelanin obtained by the action of fuming nitric acid on casein or scrapings of horn.

The action of bromine on tyrosine in presence of water yields two substances, one soluble and the other insoluble in 95 per cent. alcohol; on fusion with potassium hydroxide, these give a distinct odour of

indole or scatole, and in their method of preparation and isolation and in most of their reactions correspond with compounds (bromoproteinchrome) prepared by the action of bromine on the products of pancreatic digestion.

The small quantities of these products obtained have not allowed of their complete analysis, and the investigations are being continued.

T. H. P.

Products of Papain and Bromelin Proteolysis. By LAFAYETTE B. MENDEL and F. P. UNDERHILL (*Proc. Amer. Physiol. Soc.*, 1900, xiii—xiv).—Papain shows proteolytic activity in both alkaline and slightly acid media. The primary products correspond closely to those obtained from peptic digestions. Leucine, tyrosine, and tryptophan do not occur if bacteria are excluded. Bromelin, on the other hand, readily forms leucine, tyrosine, and tryptophan, even in acid media.

W. D. H.

Aromatic Boron Compounds. By AUGUST MICHAELIS (*Annalen*, 1901, 315, 19—43. Compare Abstr., 1894, i, 190).—[With G. THEVÉNOT].—*m*-Xylylborochloride, $C_6H_3Me_2 \cdot BCl_2$, prepared by heating *m*-mercurydixyl with boron chloride at 200° during 24 hours, is a colourless liquid which fumes in air and boils at 218° . *m*-Xylylboroxide, $C_6H_3Me_2 \cdot BO$, obtained on adding the chloride to water, forms white needles and melts at 202° . Boiling water converts the oxide into *m*-xylylboric acid, $C_6H_3Me_2 \cdot B(OH)_2$, of which the diethyl salt boils at 160° ; the hydrogen silver salt is pale yellow.

p-Xylylborochloride is a colourless liquid which boils at 205° and fumes in air. *p*-Xylylboric acid crystallises from hot water in aggregates of slender needles, and melts at 186° ; the oxide melts at 176° .

o-Xylylborochloride melts at 0° , and boils at 212° . *o*-Xylylboric acid crystallises from water in colourless, slender needles, and melts at 190.5° ; the oxide melts at 226° .

[With E. RICHTER].—A study of the following compounds necessitated the preparation of boron bromide; details of this operation are included in the paper, which also contains an illustration of the apparatus employed.

Phenylborobromide, $BPhBr_2$, prepared by heating mercurydiphenyl with boron bromide and benzene in a reflux apparatus provided with a calcium chloride tube, crystallises in colourless plates, melts at 32 — 34° , and boils at 99 — 101° under 20 mm. pressure; the compound has a penetrating odour, and fumes on exposure to air. Water decomposes it vigorously, forming phenylboric acid. *Diphenylborobromide*, BPh_2Br , a bye-product in the preparation of the foregoing substance, forms a colourless, crystalline mass which rapidly becomes red in air; it melts at 24 — 25° , and boils at 150 — 160° under 8 mm. pressure. Water converts it into diphenylboric acid.

p-Tolylborobromide, $C_6H_4Me \cdot BBr_2$, melts at 44 — 45° , and boils at 145° under 25 mm. pressure; it fumes in air, and yields *p*-tolylboric acid under the influence of water. *p*-Tolylboroxide, $C_6H_4Me \cdot BO$, produced when *p*-tolylboric acid is exposed to a dry atmosphere, melts at 257 — 258° .

m-Xylylborobromide, $C_6H_3Me_2 \cdot BBr_2$, is a colourless, refractive liquid which boils at 125° under 15 mm. pressure, and has a sp. gr. 1.57 at 15° .

ψ -Cumylborobromide, $C_6H_2Me_3 \cdot BBr_2$, is a colourless liquid which boils at 170 – 190° under 16 mm. pressure, a portion undergoing decomposition in the process; water converts it into ψ -cumylboroxide, $C_6H_2Me_3 \cdot BO$, which crystallises from ether in lustrous, white needles and melts at 211° .

p-Borobenzoic acid, $CO_2H \cdot C_6H_4 \cdot B(OH)_2$, prepared by oxidising an alkaline solution of tolylboric acid with potassium permanganate, crystallises from hot water in lustrous, white, highly refractive needles which melt at 225° ; it does not yield the anhydride when heated, merely volatilising at 125° , but when heated rapidly, the substance is resolved into benzoic acid, boric anhydride, and water. On treating a hot, aqueous solution of borobenzoic acid with mercuric chloride, chloromercuribenzoic acid, $HgCl \cdot C_6H_4 \cdot CO_2H$, is produced, forming a white, crystalline powder which melts at 272° , and dissolves in absolute alcohol; it is insoluble in water, but dissolves in aqueous alkalis.

The barium salt of *p*-borobenzoic acid contains $1H_2O$, and is more readily soluble in cold water than in hot; the lead and silver salts are amorphous.

Diphenylboric acid, $BPh_2 \cdot OH$, is difficult to obtain in the purified state; it is a colourless liquid having a powerful smell, and boils at 215 – 235° under 17 mm. pressure. The anhydride of *p*-ditolylboric acid, $[(C_6H_4Me)_2B]_2O$, prepared by heating mercuryditolyl with boron bromide and benzene and treating the product with water, separates from the latter as a white, crystalline powder and melts at 78° .

[With F. HILLRINGHAUS].—Phenyl borate, $B(OPh)_3$, prepared by heating phenol (3 mols.) with boron chloride and benzene in a sealed tube at 100° during 12 hours, is a colourless, crystalline substance; it melts very readily, and is resolved by water into phenol and boric acid. *m*-Tolyl borate, $B(O \cdot C_6H_4Me)_3$, melts at 40° , and β -naphthyl borate, $B(O \cdot C_{10}H_7)_3$, crystallises from benzene in colourless leaflets and melts at 115° .
M. O. F.

Action of Mercuric Oxide on some Organic Substances.
By ALPHONSE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Compt. rend.*, 1901, 132, 635–637).—Compounds analogous to sodium mercuri-phenoldisulphonate (this vol., i, 244) seem to be generally formed by substances containing phenolic hydroxyl, unless, like the aminophenols, they undergo oxidation. They are, however, not formed by compounds, such as anisole and phenetole, in which the hydrogen of the hydroxyl group is replaced, or by substances, like trinitrophenol and *s*-trichlorophenol, in which the ortho- and para-positions are occupied. Sodium mercuriguaiacolsulphonate has been prepared; its properties are similar to those of the corresponding phenol compound. The constitutions $Hg_2[O \cdot C_6H_3(SO_3Na)_2]_2$ or $C_6H_2(SO_3Na)_2 < \overset{O}{\underset{Hg}{\text{C}}}$ are suggested for the latter derivative.
N. L.

Organic Chemistry.

Addition of Hydrogen and other Simple Molecules to Unsaturated Compounds. By EMIL ERLÉNMEYER, jun. (*Annalen*, 1901, 316, 43—56).—A theoretical discussion as to the mode in which molecules of hydrogen and other elements and compounds combine with unsaturated carbon compounds (compare Thiele, *Abstr.*, 1899, i, 554). G. T. M.

Intramolecular Migration and its Explanation based on the Intramolecular Mobility of Multivalent Elements. By EMIL ERLÉNMEYER, jun. (*Annalen*, 1901, 316, 75—88).—A theoretical discussion not suitable for abstraction. G. T. M.

Heptane from Coniferous Trees. By W. C. BLASDALE (*J. Amer. Chem. Soc.*, 1901, 23, 163—164).—Thorpe (*Trans.*, 1879, 35, 297) has shown that the substance obtained by distillation from the exudation of *Pinus Sabiniana* consists of *n*-heptane. The author has confirmed this, and has found that *n*-heptane is also furnished by the resinous secretion of *P. Jeffreyi*, whilst those of *P. Murrayana*, *Abies concolor* v. *Lowiana* and *Pseudotsuga taxifolia* yield terpenes similar to those obtained from other coniferous trees. E. G.

The Chemistry of Methylene. By VICTOR THOMAS (*Compt. rend.*, 1901, 132, 1118—1121).—The compounds described by Sakurai (*Trans.*, 1880, 37, 658, and 1881, 39, 485) as obtained by the action of mercury on methylene iodide are formed at the ordinary temperature even in complete absence of iodoform or mercurous iodide. If mercury is heated at 190—200° in sealed tubes with methylene iodide, a mixture of methane and ethane is obtained; if the methylene iodide is heated with silver at 100° to 150°, the gaseous products contain a considerable proportion of acetylene. It would seem that methylene, CH₂, splits up into CH and H, the former condensing to form acetylene, whilst the latter unites with undecomposed methylene to form methane and ethane. C. H. B.

Formation of Chloroform from Lactic Acid. By OTTO EBERHARD (*Zeit. öffentl. Chem.*, 1901, 7, 125—126).—By the action of the calculated quantity of bleaching powder containing 23 per cent. of available chlorine, mixed with 10 times its weight of water, on lactic acid, chloroform is obtained. The equation $2[\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}_2]_2\text{Ca} + 12\text{CaOCl}_2 = (\text{CHO}_2)_2\text{Ca} + 2\text{CHCl}_3 + 9\text{CaCl}_2 + 5\text{H}_2\text{O} + 3\text{CaCO}_3 + \text{CO}_2 + (\text{C}_2\text{H}_3\text{O}_2)_2\text{Ca}$ best represents the quantities of chloroform and formic acid produced. With bleaching powder above 25 per cent. strength, the yield of chloroform becomes less. K. J. P. O.

Action of Acid Chlorides on Ethers in Presence of Zinc Chloride. By MARCEL DESCUDÉ (*Compt. rend.*, 1901, 132, 1129—1131).—When ethyl ether is heated with acetyl chloride in presence of zinc chloride, ethyl chloride is obtained in quantity corresponding with the

equation $\text{CH}_3 \cdot \text{COCl} + \text{Et}_2\text{O} = \text{C}_2\text{H}_5\text{Cl} + \text{CH}_3 \cdot \text{CO}_2\text{Et}$. Methyl amyl ether, under similar conditions, yields methyl chloride and amyl acetate, together with amyl chloride and methyl acetate. C. H. B.

Psylla Wax, Psyllostearyl Alcohol, and Psyllostearic Acid (Psylla Alcohol and Psyllic Acid). III. By ERNST EDW. SUNDWICK (*Zeit. physiol. Chem.*, 1901, **32**, 355—360. Compare Abstr., 1893, i, 125; 1898, i, 617).—Psylla wax is an ester of the composition $\text{C}_{33}\text{H}_{67} \cdot \text{O} \cdot \text{C}_{33}\text{H}_{65}\text{O}$. It is hydrolysed by hydrobromic acid, and the products are best separated, first, by solution in chloroform, and then by addition of strong sodium hydroxide to the alcoholic solution, both alcohol and acid are deposited, the latter in the form of its sodium salt, and may then be obtained by the aid of chloroform, ether, or benzene.

Psyllostearic acid, $\text{C}_{33}\text{H}_{66}\text{O}_2$, crystallises in glistening plates, melts at 94—95°, and is sparingly soluble in ether or light petroleum. *Psyllostearyl alcohol*, $\text{C}_{33}\text{H}_{67} \cdot \text{OH}$, melts at 68—70°, is soluble in light petroleum, and readily absorbs water. Its *benzoate* melts at 68—69°.

J. J. S.

Study of the Perkin Reaction. By ARTHUR MICHAEL [with ROBERT N. HARTMAN] (*Ber.*, 1901, **34**, 918—930).—When acetic anhydride is heated for half an hour on the water-bath with dried sodium butyrate, *isohexoate*, or *n*-hexoate, the higher anhydride is produced in almost theoretical yield; there seems to be no tendency to form the mixed anhydride, and the process furnishes a ready means of preparing the anhydrides of the acids of the acetic series. A similar reaction takes place with sodium propionate, but the yield of pure propionic anhydride is smaller, owing to the fact that its boiling point is very close to that of its lower homologue. The reverse action occurs when sodium acetate is heated with propionic anhydride at 130°, the product consisting of a mixture of acetic and propionic anhydrides. With sodium acetate and butyric anhydride, there is no interaction at 150°; at 180°, however, an almost complete double decomposition takes place, and the volatile product consists practically of acetic anhydride.

When mol. proportions of benzaldehyde, butyric anhydride, and sodium acetate are heated for 225 hours at 100°, a mixture of cinnamic and phenylangelic acids is produced, containing 1 part of the former to 14 of the latter, 1 part of cinnamic acid and 2 parts of its homologue being obtained when acetic anhydride and sodium butyrate are employed.

Benzaldehyde, when condensed with sodium acetate and *n*-hexoic anhydride, yields 1 part of cinnamic acid and 5 parts of *α*-butylcinnamic acid; these acids are formed in the ratio 5 : 9 when sodium hexoate and acetic anhydride are employed. *α*-Butylcinnamic acid crystallises from dilute alcohol in lustrous leaflets and melts at 83—84°. Benzaldehyde, acetic anhydride, and sodium *isohexoate*, when heated together for 100 hours at 100° and 130 at 108°, yield a mixture of cinnamic acid (2 parts) and *isobutylcinnamic acid* (3 parts); the latter compound forms lustrous, flattened needles melting at 73°; it is readily soluble in hot water and the ordinary organic solvents. G. T. M.

Condensation Products of Aliphatic Nitro-compounds. By ROLAND SCHOLL (*Ber.*, 1901, **34**, 862—869. Compare Dunstan and Goulding, *Trans.*, 1900, **77**, 1262).—It is suggested that in the formation of anhydro-compounds and condensation products from aliphatic nitro-compounds, the first stage consists in the formation of an *iso*-nitroso-compound, $>\text{CH}\cdot\text{NO}_2 \rightarrow >\text{C}:\text{NO}\cdot\text{OH}$, and that this is followed by the elimination of water, either from one mol. of the substance to form an *oxynitrile*, $\text{R}\cdot\text{CH}:\text{NO}\cdot\text{OH} \rightarrow \text{R}\cdot\text{C}:\text{N}:\text{O}$, or from two mols. $2\text{R}\cdot\text{CH}:\text{NO}\cdot\text{OH} \rightarrow \text{R}\cdot\text{CH}:\text{NO}\cdot\text{CR}\cdot\text{NO}\cdot\text{OH}$, to form a condensation product. In accordance with these views, methazonic acid is regarded as a nitrogen analogue of acetoacetic acid, $\text{CH}_3:\text{NO}\cdot\text{CH}:\text{NO}\cdot\text{OH}$, and cyanomethazonic acid as $\text{CN}\cdot\text{CH}:\text{NO}\cdot\text{C}(\text{CN}):\text{NO}\cdot\text{OH}$ or $\text{CN}\cdot\text{CH}:\text{NO}\cdot\text{CH}(\text{CN})\cdot\text{NO}_2$.

The compounds described in the following abstract are also regarded as products of this type of change. T. M. L.

Action of Ethyl Bromoacetate on Silver Nitrite. By ROLAND SCHOLL and ALWIN SCHÖFER (*Ber.*, 1901, **34**, 870—881).—From the interaction of ethyl bromoacetate and silver nitrite, ethyl glycollate, ethyl ethoxyacetate, ethyl glycollate nitrite and nitrate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}$ and $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}_2$, diethyl oxalate, ethyl oxynitriloformate, ethyl dioxycyano-gendicarboxylate, and a compound $\text{C}_{12}\text{H}_{15}\text{O}_8\text{N}$, are obtained.

Ethyl oxynitriloformate, $\text{CO}_2\text{Et}\cdot\text{C}:\text{N}:\text{O}$, crystallises from hot benzene in colourless needles, melts at $111-111.5^\circ$, has a normal molecular weight as determined from the freezing point of a solution in acetic acid, and is probably formed by the loss of 1 mol. of water from ethyl dioxynitroacetate.

Ethyl dioxycyano-gendicarboxylate, a polymeride of the preceding compound, regarded as having the constitution $\text{CO}_2\text{Et}\cdot\text{C} \begin{smallmatrix} \text{N}(\text{:O}) \\ \text{N}(\text{:O}) \end{smallmatrix} \text{C}\cdot\text{CO}_2\text{Et}$, boils at 158° (corr.) under 11 mm., and at $233-234^\circ$ under atmospheric pressure, and is reduced by tin and hydrochloric acid to aminoacetic acid. The *potassium* salt, $\text{C}_2\text{N}_2\text{O}_2(\text{CO}_2\text{K})_2\cdot 3\text{H}_2\text{O}$, prepared by hydrolysis of the ester with ice-cold potassium hydroxide, is readily converted into potassium oxalate by the further action of potassium hydroxide, and explodes at 92° . The *acid*, $\text{C}_4\text{H}_2\text{O}_6\text{N}_2$, crystallises in needles and explodes at 70° or when rubbed on a rough surface. The *amide*, $\text{C}_2\text{N}_2\text{O}_2(\text{CO}\cdot\text{NH}_2)_2$, is only slightly soluble in most solvents, but crystallises from a large bulk of hot water in a snow-like form, and decomposes at $120-121^\circ$, with evolution of gas, to a liquid which solidifies on cooling (? oxamide). The *methylamide* crystallises from alcohol in needles and melts at 162° . The *benzylamide* crystallises from alcohol and melts at $174-175^\circ$. The *allylamide* is a crystalline powder melting at $95-97^\circ$. The *diethylamide* crystallises from hot alcohol in small needles and decomposes at 167° , with evolution of gas.

The *compound*, $\text{C}_{12}\text{H}_{15}\text{O}_8\text{N}$, is an oil boiling at $188-189^\circ$ under 11 mm. pressure; it gives an amide by the action of strong ammonia, and is regarded as having the constitution $\text{C}_3\text{O}_2\text{N}(\text{CO}_2\text{Et})_3$. T. M. L.

Two New Acids of the Acetylene Series. Synthesis of Octoic and Pelargonic Acid. By CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1901, **132**, 988—990).—*Amylpropionic* [*a-octinoic*] acid,

$C_5H_{11} \cdot C:C \cdot CO_2H$, prepared by treating sodium heptinene with carbon dioxide, is a colourless, viscid liquid, boiling at $149-149.5^\circ$ under 20 mm. pressure, and having a sp. gr. 0.9677 at 18° ; it solidifies in ice and then melts at 5° . When heated at $180-220^\circ$, the acid decomposes into carbon dioxide and heptinene. *Amylpropionic chloride*, obtained by treating the preceding compound with phosphorus pentachloride, boils at $88-89^\circ$ under 17 mm. pressure, and has a sp. gr. 1.0202 at 0° . The *o-toluidide* of amylpropionic acid, produced by mixing the chloride with *o*-toluidine, melts at $59.5-60.5^\circ$; the *p-toluidide*, *p-anisidide*, and *α -naphthylamide*, melt respectively at 68° , 44° , and $113-114^\circ$.

The esters of amylpropionic acid are prepared either by treating sodium heptinene with the alkyl chlorocarbonates, or by the interaction of amylpropionic chloride and the corresponding alcohol. When a mixture of amylpropionic acid and an alcohol is saturated with hydrogen chloride, the main product of reaction is the corresponding ester of the acid, $C_5H_{11} \cdot CCl:CH \cdot CO_2H$.

Amylpropionic acid takes up four atoms of bromine, but the addition of the last two is a matter of some difficulty, and the reaction is always attended by an evolution of hydrogen bromide; on the other hand, the acid is readily reduced to a fully saturated acid, identical in its properties with octoic acid.

Hexylpropionic [noninoic] acid, $C_6H_{13} \cdot C:C \cdot CO_2H$, is a colourless, viscid liquid having a sp. gr. 0.9644 at 0° ; it solidifies in liquid methyl chloride and melts at -10° . When treated with sodium and boiling absolute alcohol, the compound is completely reduced, yielding pelargonic acid.

The following ethereal salts of these unsaturated acids are described in the paper:

| Ester. | B. p. | Sp. gr. at 0° . |
|----------------------------|--------------------------|------------------------|
| Methyl amylpropiolate ... | 107° under 20 mm. | 0.9524 |
| Ethyl " ... | $115-116.5^\circ$ " 17 " | 0.9395 |
| <i>iso</i> Propyl " ... | $126-127^\circ$ " 22 " | 0.9183 |
| <i>iso</i> Butyl " ... | $138-139^\circ$ " 23 " | 0.916 |
| <i>iso</i> Amyl " ... | $148-149^\circ$ " 20 " | 0.9114 |
| Allyl " ... | $124-128^\circ$ " 18 " | 0.9465 |
| Methyl hexylpropiolate ... | 122° " 19 " | 0.9338 |
| Ethyl " ... | $126-128^\circ$ " 16 " | 0.9223 |

G. T. M.

Hydrogenation of Amylpropionic Acid; Hexoylacetic Acid. By CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1901, 132, 1121-1124).—Amylpropionic acid (preceding abstract) is but slightly attacked by concentrated sulphuric acid, but if about 3 per cent. of sulphur trioxide is added there is an energetic reaction with formation of hexoic acid and a sulphonic acid, the barium salt of which forms slender needles slightly soluble in water.

If the acid is boiled with alcoholic potash, it yields *hexoylacetic acid*, $CH_3Me \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO_2H$, which crystallises in white lamellæ and decomposes slowly at the ordinary temperature and rapidly at 60° into carbon dioxide and methyl amyl ketone. Its *methyl* and

ethyl esters are more stable; the former boils at 115—116° under 14 mm. pressure and has a sp. gr. 0.994 at 0°, and the latter boils at 126—127° under 19 mm. pressure and has a sp. gr. 0.9721 at 0°. The sodium derivatives of the esters are white and insoluble; the copper derivatives are very soluble in chloroform and crystallise from alcohol in minute prisms, the derivative of the methyl ester melting at 113—114° and that of the ethyl ester at 107°.

When the chlorine derivatives of the esters of amylpropionic acid are heated with alcoholic potash, they yield methyl amyl ketone amongst other products, and this establishes the constitution already attributed to this acid. C. H. B.

Formylacetic Esters. By WILHELM WISLIGENUS and WILLI BINDEMANN (*Annalen*, 1901, 316, 18—42. Compare Abstr., 1887, 129).—The esters of formylacetic acid and their metallic derivatives have not been isolated in a pure state owing to their tendency to undergo condensation.

Ethyl formylglutaconate (*ethyl hydroxymethyleneglutaconate*), $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, results from the action of dilute sulphuric acid on the sodium derivative of ethyl formylacetate dissolved in ether, and is best extracted from solution in the form of its copper derivative; it crystallises from ether in colourless plates and melts at 66—67°. The ester is readily soluble in the ordinary organic solvents and in sodium hydroxide solution; it cannot be distilled; its alcoholic solution develops a bluish-violet coloration with ferric chloride.

After some time, this compound changes into an oily modification, which gives a red coloration with ferric chloride. This transformation is accelerated either by the action of heat or by dissolving the substance in dilute methyl alcohol or ether; it is, however, prevented by keeping the ester in the presence of benzene. This transformation is similar to that noticed in the case of ethyl formylphenylacetate (Abstr., 1887, 129), excepting that benzene does not convert the oily form of ethyl formylglutaconate into the original solid modification. The oily form of the glutaconate slowly condenses to ethyl trimesate, this reaction being accelerated by distilling under a pressure of 1 mm. The copper derivative of ethyl formylglutaconate crystallises from benzene in moss-green leaflets and melts at 167—168°; it is far more stable on keeping than the free ester.

A pyrazole derivative, $\text{C}_{16}\text{H}_{18}\text{O}_4\text{N}_2$, having a constitution corresponding with either $\text{N} \begin{array}{c} \text{NPh} \cdot \text{CH} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} \\ \text{CH} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$ or $\text{NPh} \begin{array}{c} \text{N} = \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} \\ \text{CH} : \text{C} \cdot \text{CO}_2\text{Et} \end{array}$ is obtained by the action of phenylhydrazine on ethyl formylglutaconate, the condensation being accompanied by the elimination of hydrogen and water; it separates from benzene in prismatic crystals, melts at 89—90°, and boils at 230—235° without decomposition; its solution in concentrated sulphuric acid does not develop a coloration with ferric chloride or potassium dichromate.

The crude sodium derivative of ethyl formylacetate, when boiled with excess of dilute sulphuric acid, partly condenses to trimesic acid, and partly decomposes into alcohol, acetaldehyde, and carbon dioxide.

The *phenylhydrazone* of ethyl formylacetate, $\text{N}_2\text{HPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$,

obtained by the action of phenylhydrazine hydrochloride on the sodium derivative of ethyl formylacetate dissolved in water, crystallises from alcohol in yellow needles and melts at 54—57°; it changes on keeping into a dark coloured, tarry substance, and when boiled with toluene yields the compound melting at 173—174° previously described by Stolz (Abstr., 1895, i, 398).

Ethyl 1-phenylpyrazole-4-carboxylate, $\text{CO}_2\text{Et} \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{NPh} \\ \text{CH} \cdot \text{N} \end{smallmatrix}$, produced by distilling the preceding compound under 14 mm. pressure, crystallises from absolute alcohol in lustrous prisms and melts at 96—97°; it does not develop a coloration with ferric chloride either in alcoholic or in concentrated sulphuric acid solution. On hydrolysis with alcoholic sodium hydroxide, the ester yields the acid melting at 219—220° (compare Abstr., 1893, i, 672; 1897, i, 440).

The sodium derivative of ethyl formylacetate yields two isomeric *p*-nitrobenzoates according as to whether the reaction is carried out in ether or in water. The α -compound is formed by the action of *p*-nitrobenzoyl chloride on the sodium derivative suspended in ether; it crystallises from ether in needles melting at 87—88°; the β -isomeride is produced in aqueous solution and crystallises from ether in light red, flattened plates melting at 92—93°. Both compounds can be distilled under reduced pressure without decomposition and they give the ferric chloride reaction.

The sodium derivative of methyl formylacetate is obtained as a white powder by treating with sodium a mixture of methyl acetate and formate dissolved in dry ether; the free ester could not be isolated.

Methyl formylglutaconate, $\text{OH} \cdot \text{CH} \cdot \text{C}(\text{CO}_2\text{Me}) \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{Me}$ (Abstr., 1893, i, 402) results from the action of sulphuric acid on the preceding compound; like its ethyl homologue, it slowly changes into an oily modification which develops a red coloration with ferric chloride, this transformation being accelerated by warming. This change is also accompanied by a condensation which results in the formation of methyl trimesate.

The *phenylhydrazone* of methylformylphenylacetate, $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2$, separates from methyl alcohol in yellow crystals and melts at 47°, it darkens on keeping, and on boiling with toluene yields a compound, $\text{C}_{22}\text{H}_{20}\text{O}_4\text{N}_4$, crystallising in white leaflets from methyl alcohol and melting at 183—184°.

Methyl 1-phenylpyrazole 4-carboxylate, $\text{CO}_2\text{Me} \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{N} \\ \text{CH} \cdot \text{NPh} \end{smallmatrix}$, obtained by distilling the preceding hydrazone under diminished pressure, crystallises from methyl alcohol in colourless needles and melts at 128—129°; it gives the pyrazoline reaction and yields the corresponding acid on hydrolysis.

The amyl esters of acetic and formic acids, when dissolved in ether, and treated with sodium, yield the sodium derivative of amyl formylacetate; on treatment with acid the free ester separates as an oil giving the ferric chloride reaction and yielding *amyl trimesate* on distillation under 15 mm. pressure.

G. T. M.

New Reactions of Organometallic Derivatives. III. Unsubstituted β -Ketonic Esters. By EDMOND E. BLAISE (*Compt. rend.*, 1901, 132, 978—980. Compare this vol., i, 252).—The interaction between ethyl cyanoacetate and the ether additive compounds of the magnesium alkyl iodides ($R \cdot MgI, Et_2O$), followed by the decomposition of the intermediate products by the addition of water, furnishes a general method for the preparation of the unsubstituted β -ketonic esters, $R \cdot CO \cdot CH_2 \cdot CO_2Et$.

Ethyl propionylacetate and *butyrylacetate* are liquids developing red colorations with ferric chloride; sodium hydrogen sulphite combines with the former but not with the latter; the higher homologue being isolated by means of its *magnesium* derivative, a well-defined substance crystallising from methyl alcohol in needles, and melting at $156-157^\circ$. Ethyl acetoacetate, when reacting with semicarbazide, yields a semi-carbazone, whereas its homologues undergo further condensation, giving rise to the amides of the corresponding pyrazolonecarboxylic acids; these compounds develop intense blue colorations with alcoholic solutions of ferric chloride. Phenylhydrazine reacts with these esters, forming pyrazolones, excess of the reagent giving rise to bispyrazolones; the latter compounds crystallise readily from a mixture of formic acid and alcohol, and are readily converted into pyrazole-blues on oxidation with potassium ferricyanide in alkaline solution.

Ethyl propionylacetate boils at $91-92^\circ$ under 17 mm. and at 191° under atmospheric pressure; 3-*Ethylpyrazolone-1-carboxylamide*, $NH_2 \cdot CO \cdot N \begin{smallmatrix} N=CEt \\ \diagdown \\ CO \cdot CH_2 \end{smallmatrix}$, melts at 197° , but decomposes slowly when maintained at 172° . 1-*Phenyl-3-ethylpyrazolone* melts at 100° and develops a red coloration with alcoholic ferric chloride.

Bisphenylethylpyrazolone, $(NPh \begin{smallmatrix} N=CEt \\ \diagdown \\ CO \cdot CH_2 \end{smallmatrix})_2$, melts at 335° , and when oxidised yields the blue compound, $(NPh \begin{smallmatrix} N=CEt \\ \diagdown \\ CO \cdot C: \end{smallmatrix})_2$, which separates from acetic acid in brownish-black crystals and melts at 234° .

Ethyl butyrylacetate boils at 104° under 22 mm. pressure, 3-*propylpyrazolone-1-carboxylamide* melts at 189° , and 1-*phenyl-3-propylpyrazolone* at $109-110^\circ$. The corresponding *bispyrazolone* does not melt below 335° , and its oxidation product crystallises from ethyl acetate in bluish-black needles and melts at 191° . G. T. M.

Action of Ethereal Alkylcyanoacetates on Diazonium Chlorides. By G. FAVREL (*Compt. rend.*, 1901, 132, 983—985. Compare *Abstr.*, 1900, i, 532).—The *phenylhydrazone*, $NHPh \cdot N: CMe \cdot CN$, of the nitrile of pyruvic acid is obtained by treating a solution of benzene-diazonium chloride with methyl cyanomethylacetate and sodium hydroxide, its formation being accompanied by the elimination of methyl alcohol and carbon dioxide; it crystallises from benzene in lamellæ, and melts at $150-151^\circ$. This substance, when heated with sodium hydroxide dissolved in dilute alcohol, yields the phenylhydrazone of pyruvic acid.

The *p*- and *o*-tolylhydrazones produced from methyl cyanomethylacetate, and the corresponding diazonium salts, melt respectively at 166—167° and 131—132°.

The *phenylhydrazone*, $\text{NHPh}\cdot\text{N}:\text{C}(\text{Et})\cdot\text{CN}$, resulting from the interaction of ethyl cyanoethylacetate and benzenediazonium chloride, melts at 81—82°; the corresponding *p*- and *o*-tolylhydrazones melt at 143—144° and 114—115° respectively. G. T. M.

Dimethylpyruvic Acid. By A. WAHL (*Compt. rend.*, 1901, 132, 1124—1126).—When dimethylpyruvic esters are treated with ammonia, the product is not dimethylpyruvamide, but a neutral crystallisable compound which melts at 198°, and can also be obtained by heating ethylaminodimethylacrylate with water in sealed tubes at 130—140°.

Attempts to decompose the acid by heating it with aniline, to convert it into isobutaldehyde by the action of dilute sulphuric acid, and to oxidise it by means of silver oxide gave negative results.

When treated with sodium amalgam in presence of dilute alcohol, it is converted into α -hydroxyisovaleric acid, and this definitely determines its constitution. C. H. B.

Methyladipic Acid from the Oxidation of Pulegone and β -Methylcyclohexanone. By LOUIS BOUVEAULT and LÉON ALEXANDRE TETRY (*Bull. Soc. Chem.*, 1901, [iii], 25, 441—444).—Contrary to the statement of Markownikoff (*Abstr.*, 1900, i, 475), the authors find that the oxidation of β -methylcyclohexanone by nitric acid results in the formation, not of α -methyladipic acid, but of the β -acid, which was identified by means of its dianilide, melting at 198—199°. α -Methyladipic acid forms a *dianilide* crystallising in slender, white needles melting at 168°, and a *monoanilide* which forms small, white crystals melting at 122°. Adipic acid yields a *dianilide* which crystallises in small, white needles melting at 235°. These dianilides are readily prepared and purified, and are well adapted for the identification, and even the separation, of the corresponding acids. N. L.

Synthesis of the $\alpha\alpha'$ -Dimethyladipic Acids. By OTTO MOHR (*Ber.*, 1901, 34, 807—813).—The action of hydrogen bromide on diallyl or on methylbutallylcarbinol, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, yields along with the solid $\beta\zeta$ -dibromohexane melting at 38.2° (Demjanoff, *Abstr.*, 1891, 160) a liquid *stereoisomeride*, which boils at 94° under 13—14 mm. pressure, and does not solidify in a freezing mixture of ether and solid carbon dioxide. Both forms of $\beta\zeta$ -dibromohexane, on converting into the corresponding nitriles by boiling for 4 hours with dilute alcoholic potassium cyanide and hydrolysing with alcoholic potassium hydroxide, yield identical products. In each case, the portion which is not volatile with steam consists of nearly equal parts of the two $\alpha\alpha'$ -dimethyladipic acids, melting at 143.5° and 75—77° respectively (Zelinsky, *Abstr.*, 1892, 430); the part volatile with steam is an acid oil which, when strongly cooled, yields crystals of *α -methyl- δ -hexolactone*, $\text{CHMe}\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{O} \end{smallmatrix}\rangle\text{CHMe}$, melting at 58—59°, and easily dissolving in warm baryta water to form a crystalline barium *α -methyl- δ -hydroxyhexoate*. The oil remaining after the separa-

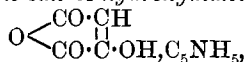
tion of the lactone boils at 220—250°, combines additively with bromine, decolorises alkaline potassium permanganate, and is probably a mixture of α -methyl- γ -hexenoic acid and δ -ethoxy- α -methylhexoic acid, $\text{OEt} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe}_2 \cdot \text{CO}_2\text{H}$.

The dimethyladipic acid melting at 75—77° is largely converted into its isomeride of higher melting point when heated with water or dilute ammonia for a long period; the reverse transformation is only partially brought about by heating the form melting at 143.5° with water, either alone or with traces of ammonia, piperidine, or aniline. W. A. D.

Undecanedicarboxylic Acid and the Electrosynthesis of Decanedicarboxylic Acid. By GUSTAV KOMPPA (*Ber.*, 1901, 34, 895—902).—Krafft and Seldis (*Abstr.*, 1901, i, 115) did not obtain the same undecanedicarboxylic acid, when they carried out the author's synthesis of undecane- $\alpha\lambda$ -dicarboxylic acid (*Abstr.*, 1900, i, 201). The author has repeated his experiments and obtains the same results. The melting point of the amide of undecane- $\alpha\lambda$ -dicarboxylic acid is 155—156° (not 150.5°). R. H. P.

Conversion of Tartaric Acid into Oxalacetic Acid by the Removal of Water at Low Temperatures. By ALFRED WOHL and CARL OESTERLIN (*Ber.*, 1901, 34, 1139—1148).—*Basic pyridine diacetyltartrate*, $\text{C}_8\text{H}_{10}\text{O}_8 \cdot \text{C}_5\text{NH}_5$, obtained by the action of aqueous pyridine on diacetyltartaric anhydride, crystallises well from alcohol and melts at 121°.

When diacetyltartaric anhydride is added to anhydrous pyridine kept at -5°, the *pyridine salt of hydroxymaleic anhydride*,



is obtained; better yields are obtained in presence of pyridine acetate. The compound melts at 108—110°, is optically inactive, and when treated with double the theoretical quantity of 12 per cent. sulphuric acid, yields an oxalacetic acid which is identical in its properties and in those of its methyl ester with the acid obtained by Fenton and Jones (*Trans.*, 1900, 77, 77), except that it melts at 146°, whilst Fenton and Jones' acid has the melting point 176°. If the strength of the acid used in decomposing the pyridine salt be 30 per cent. instead of 12 per cent., an oxalacetic acid melting at 176° is obtained. This acid of higher melting point is readily transformed into that of lower by heating in aqueous solution with pyridine, acidifying with 12 per cent. sulphuric acid, extracting with ether, and crystallising.

On treating the pyridine salt of hydroxymaleic anhydride with aniline at the ordinary temperature, solution takes place with considerable heating and vigorous evolution of carbon dioxide, and on adding dilute hydrochloric acid, the anilide of pyruvic acid is obtained. When suspended in benzene and treated with acetyl chloride, the pyridine salt yields acetoxy maleic anhydride. T. H. P.

Action of Alcohols on the Acetals of Monohydric Alcohols. By MARCEL DELÉPINE (*Compt. rend.*, 1901, 132, 968—971. Compare this vol., i, 3, 254, 314; ii, 6).—When an acetal is boiled with an alcohol in the presence of a few drops of hydrochloric acid, a

double decomposition takes place, resulting in the formation of two new aldehyde ethers. The reaction is a balanced one, the product containing, in addition to the new compounds, a certain quantity of the reagents, together with the corresponding amount of the alcohol formerly combined with the original acetal. Whether methylal is heated with amyl alcohol or diamylformal with methyl alcohol, the result is the same, the product consisting of a mixture of methylal, diamylformal, methyl and amyl alcohols, and the mixed acetal, $\text{OMe} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_5\text{H}_{11}$. Similar results are obtained with the following pairs of reagents: ethylalcohol and diamylformal, methyl alcohol and dipropylformal, propyl alcohol and methylal. The products always contain five compounds, those of higher molecular weight predominating. When methyl or butyl alcohol reacts with diethylchloroacetal, a mixture of three chloroacetals is produced, consisting chiefly of the mixed ether; the compound, $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OEt}) \cdot \text{OC}_4\text{H}_9$, boils at $190-195^\circ$.

β -Naphthol reacts with the acetals, giving rise to compounds containing the aldehydic residue directly attached to the aromatic nuclei, methylal yielding 2:2'-dihydroxy-1:1'-dinaphthylmethane, whilst the anhydride of the corresponding ethane derivative, $\text{CHMe}:(\text{C}_{10}\text{H}_6)_2\text{O}$, is obtained from acetal. Chloroacetal also gives rise to an anhydride, $\text{CH}_2\text{Cl} \cdot \text{CH}:(\text{C}_{10}\text{H}_6)_2\text{O}$, this compound melting at $173-174^\circ$.

The polyhydric alcohols almost entirely displace the monohydric alcohols from their aldehyde ethers; ethylene glycol reacting on diethylchloroacetal yields the compound, $\text{CH}_2\text{Cl} \cdot \text{CH} \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \text{O} \cdot \text{CH}_2 \end{smallmatrix}$, boiling at $156-157^\circ$. Dimethylpinacone replaces methyl and ethyl alcohols in a similar manner, and in this way its *chloroacetal*, *acetal*, and *formal* ethers have been prepared; they are liquids boiling respectively at $191-192^\circ$, 134° , and $124-125^\circ$. The *chloroacetal* of glycerol boils at $235-240^\circ$. Erythritol reacting with acetal gives rise to the *diacetal* melting at 95° and the *monoacetal*, $\text{C}_4\text{H}_8\text{O}_4 \cdot \text{C}_2\text{H}_4$, melting at 102° ; its *dichloroacetal*, $\text{C}_4\text{H}_6\text{O}_4(\text{C}_2\text{H}_3\text{Cl})_2$, melts at $101-103^\circ$.

The reactions between mannitol and the acetals are more complicated, and a certain amount of the alcohol changes into mannitan; nevertheless, the *triacetal*, melting at $171-173^\circ$, was isolated from the products of reaction with acetal, whilst the *dichloroacetal*, $\text{C}_6\text{H}_{10}\text{O}_6(\text{C}_2\text{H}_3\text{Cl})_2$, melting at 135° , was obtained by the action of chloroacetal.

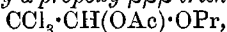
G. T. M.

Bromide and Iodide of Acetylchloral. By EMILIO GABUTTI and G. BARGELLINI (*Gazzetta*, 1901, 31, i, 82-85).—*Acetylchloral bromide* (α -bromo- $\beta\beta$ -trichloroethyl acetate), $\text{CCl}_3 \cdot \text{CHBr} \cdot \text{OAc}$, prepared by the action of acetyl bromide on chloral, is a heavy, colourless oil with a pleasant odour resembling that of the corresponding chloride; it distils undecomposed at 106° under a pressure of 735 mm. of mercury, and is extremely soluble in alcohol, ether, or chloroform, but insoluble in water. With cold dilute alkali hydroxide solutions, it has no action, but with hot concentrated solutions it yields chloroform.

Acetylchloral iodide (α -iodo- $\beta\beta$ -trichloroethyl acetate), $\text{CCl}_3 \cdot \text{CHI} \cdot \text{OAc}$, prepared from acetyl iodide and chloral, is a dense oil from which the free iodine could not be completely removed. It readily decomposes on heating, even under reduced pressure.

T. H. P.

Action of Alcohols on Chloral. By EMILIO GABUTTI (*Gazzetta*, 1901, 31, i, 86—92).—*Chloral propylate* (α -hydroxy- α -propoxy- $\beta\beta\beta$ -trichloroethane), $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{OPr}$, prepared by the action of propyl alcohol on chloral, is a dense, colourless liquid with an odour faintly recalling that of propyl alcohol; it boils at 120 — 122° , and is very soluble in alcohol or ether, but insoluble in water. The action of acetyl chloride on chloral propylate yields the following three compounds. (1) Acetylchloral chloride, (2) propyl acetate, and (3) *acetylchloral propylate* (α -acetoxy- α -propoxy- $\beta\beta\beta$ -trichloroethane),



which is a colourless liquid boiling at 114 — 116° ; it does not dissolve in water, but is extremely soluble in alcohol or ether, and has a pleasant odour recalling that of acetic acid.

Chloral isopropylate (α -hydroxy- α -isopropoxy- $\beta\beta\beta$ -trichloroethane), $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{OPr}^i$, obtained by the action of isopropyl alcohol on chloral, is a colourless liquid with an odour resembling that of isopropyl alcohol; it boils at 108° , and, on cooling with ice and salt, crystallises to a mass of small, white needles melting at 47° ; it is extremely soluble in alcohol or ether, but insoluble in water. The only compound which could be separated from the products of the action of acetyl chloride on chloral isopropylate was isopropyl acetate.

Trimethylcarbinol could not be made to react with chloral, even when the two compounds were heated together in a sealed tube at 150 — 180° . This alcohol, hence, resembles the phenols in this respect.

T. H. P.

Methyl Nonyl Ketone. By HENRI CARETTE (*J. Pharm.*, 1901, [vi], 13, 412—415).—Cinnamaldehyde condenses with methyl nonyl ketone under the action of alcoholic potash. The product forms white, lustrous needles melting at 87° . By changing the conditions, no other substance can be obtained. The author has shown that benzaldehyde and methyl nonyl ketone give more than one condensation product.

K. J. P. O.

Oxime of Diacetoneamine. By M. KOHN (*Ber.*, 1901, 34, 792—794).—The author has prepared diacetoneaminooxime (Harries, this vol., i, 194) independently by dissolving diacetoneamine oxalate in hot water, cooling, adding concentrated aqueous potassium hydroxide, and then aqueous hydroxylamine hydrochloride, both gradually and with constant shaking; the product is eventually extracted with ether and distilled under diminished pressure. When dissolved in 10 per cent. aqueous sodium hydroxide and shaken with benzoyl chloride, it readily forms a *dibenzoyl* derivative, $\text{NHBz}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{NOBz}$, which melts at 121 — 123° .

C. F. B.

Fermentation of Pentoses. By A. SCHÖNE and BERNHARD TOLLENS (*J. Landw.*, 1901, 49, 29—40).—According to Scheibler, von Lippmann, Stone and Tollens, and Lindner, arabinose does not ferment with yeast. Frankland and MacGregor (*Trans.*, 1892, 61, 737) found that *Bacillus ethaceticus* decomposes arabinose with production of alcohol, acetic, formic, and succinic acids, carbon dioxide and hydrogen.

Cross and Bevan (*Jour. Fed. Inst. Brewing*, 1897, 3, No. 1) state that during the fermentation of worts, a portion of the pentoses or pentosans disappears, along with the maltose. Salkowski (*Abstr.*, 1900, i, 628) found that arabinose, in presence of putrefying meat, was decomposed into alcohol, volatile acids (especially acetic acid), and non-volatile acids, including succinic acid. Xylose seemed to yield the same products.

Extracts (with boiling 3 per cent. sulphuric acid) of jute and brewers' grains, neutralised with calcium carbonate, were subjected to the action of lager beer yeast for some days at 26—27°. A considerable reduction in the amount of pentosans took place, and, coincidentally, alcohol and acetic and lactic acids were formed. Similar results were obtained with pure yeast (Hansen's).

In the case of pure arabinose, pure yeast had practically no effect, but an organism from sour milk decomposed arabinose, with production of alcohol and acids.

N. H. J. M.

Rhodeose, a Methylpentose from Convolvulin. By EMIL VOTOČEK (*Zeit. Zuckerind. Böhm.*, 1901, 25, 297—305. Compare *Abstr.*, 1900, i, 332).—The following derivatives of rhodeose have been prepared. The *phenylmethylhydrazone*, $C_6H_{12}O_4 \cdot N_2MePh$, separates from alcohol in colourless, silky needles melting at 181—182°. The *phenylethylhydrazone* crystallises from alcohol in shining, colourless needles melting at 193°. The *p-bromophenylhydrazone* separates from dilute alcohol in yellowish crystals which have a silky lustre and melt at 184°. The *phenylbenzylhydrazone* is deposited from alcohol in nearly white crystals melting at 178—179°.

By the action of benzaldehyde on the phenylmethylhydrazone, rhodeose is obtained, and slowly crystallises in stellate aggregates of microscopic, anhydrous needles. Aqueous solutions of the sugar show mutarotation, the final value of $[\alpha]_D$ being +75.2°; the lower number previously obtained (*loc. cit.*) seems to be due to the presence in crude rhodeose of another methylpentose having a lower rotation.

Various colour reactions of crystallised rhodeose are described. Rhodeose reduces Fehling's solution and ammoniacal silver solution; methylfurfuraldehyde is formed when a solution of the sugar is boiled with 12 per cent. hydrochloric acid solution.

T. H. P.

Refraction of Aqueous Carbohydrate Solutions. I. Mutarotating Sugars (Hexoses). By F. STOLLE (*Zeit. Ver. deut. Zuckerind.*, 1901, 335—347).—In order to obtain evidence as to the nature of the changes occurring in solutions of sugars exhibiting mutarotation, the author has determined the alteration in specific gravity, and hence in concentration and also in the refraction, of solutions of lævulose, dextrose, and galactose when kept for 24 hours. The anhydrous sugars were used and a number of solutions varying in concentration from about 1 to about 20 per cent. were examined, the temperature in all cases being 17.5°.

Seven solutions of lævulose were prepared, and the concentration (grams per 100 c.c.) at various times after making the solutions are given in the following table :

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. |
|-----------------|--------|--------|--------|--------|---------|---------|---------|
| 10 minutes..... | 1·0090 | 2·0100 | 4·0110 | 8·0073 | 12·0250 | 15·9990 | 25·0160 |
| 6 hours | 1·0091 | 2·0100 | 4·0116 | 8·0074 | 12·0263 | 15·9999 | 25·0190 |
| 24 hours | 1·0091 | 2·0105 | 4·0124 | 8·0091 | 12·0275 | 16·0055 | 25·0187 |

It will be seen that in each solution an increase takes place in the proportion of active substance present, and this is accompanied by a corresponding increase in the index of refraction as is shown by the following values of n_D for the various solutions :

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. |
|-----------------|---------|---------|---------|---------|---------|---------|---------|
| 10 minutes..... | 1·33448 | 1·33596 | 1·33872 | 1·34447 | 1·35008 | 1·35572 | 1·36825 |
| 24 hours | 1·33448 | 1·33595 | 1·33882 | 1·34456 | 1·35036 | 1·35591 | 1·36844 |

The quotient obtained by dividing the difference between the refractive index of any solution and that of water by the concentration, has a constant value of about 0·00141 for all the solutions. The specific refraction (Lorentz and Lorenz formula) of levulose in the solutions examined does not vary either with the concentration or with time, the value in all cases being about 0·206.

The results obtained with dextrose and galactose are strictly comparable with the above, the quotient of the increment of refractive index by concentration having about the same value, 0·00141 and the specific refraction being approximately 0·206.

These results are all in favour of the hydrate theory according to which the anhydrous sugar takes up a molecule of water to form the heptahydric alcohol, $C_6H_{14}O_7$, having a lower rotatory power than the sugar.

T. H. P.

Dextrose. By FERDINAND VON ARLT (*Monatsh.*, 1901, 22, 144—150).—By the action of phosphorus pentachloride on pentacetyldextrose dissolved in dry chloroform in the presence of aluminium chloride, acetochlorohydrose is obtained. It crystallises from ether in needles melting at 72—74° and having $[\alpha]_D + 165·76^\circ$ at 20°. On reduction with zinc dust and iron filings in acetic acid solution, a pentacetylhexose is obtained which appears to be identical with α -pentacetyldextrose described by Franchimont (*Abstr.*, 1893, i, 246). Hydrolysis with sulphuric acid converts it into a sugar, which yields phenylglucosazone with phenylhydrazine.

K. J. P. O.

Derivatives of Dextrose and of Galactose. By WILHELM KOENIGS and EDUARD KNORR (*Ber.*, 1901, 34, 957—981. Compare Ryan, *Trans.*, 1899, 75, 1054).—*Tetracetyl bromodextrose*, $C_6H_7OBr(OAc)_4$, obtained when dextrose (1 mol.) is treated with acetyl bromide (5 mols.), crystallises from dry ether in glistening, white needles melting at 88—89°, is readily soluble in most organic solvents, and has $[\alpha]_D + 198^\circ 10'$ at 19°. It is slowly hydrolysed by water, reduces boiling

Fehling's solution, and the bromine is as readily replaceable as the chlorine in tetracetylchlorodextrose. When its solution in glacial acetic acid is shaken with silver acetate, pentacetyldextrose is formed. With methyl alcoholic solutions of potassium phenoxide and β -naphthoxide, it yields phenylglucoside (compare Michael, Abstr., 1885, 521) and β -naphthylglucoside (Ryan). When left in contact with absolute methyl alcohol for several days, it yields β -methylglucoside melting at $108-110^\circ$ (Abstr., 1895, i, 5). When shaken with absolute methyl alcohol and dry silver carbonate, it yields *tetracetyl- β -methylglucoside*, $\text{OMe} \cdot \text{C}_6\text{H}_7\text{O}(\text{OAc})_4$. This crystallises from methyl alcohol in large, glistening, rhombic crystals [$a:b:c = 0.7634:1:0.4638$], dissolves readily in most solvents; it sinters at 102° , melts at $104-105^\circ$, has $[\alpha]_D - 23.6'$ at 15° , has no reducing action on boiling Fehling's solution, and is readily hydrolysed by alkali to β -methylglucoside. The same compound is formed when a concentrated aqueous solution of silver nitrate acts on a methyl alcoholic solution of tetracetyl bromodextrose, and also when the bromo-compound is treated with a methyl alcoholic solution of pyridine. *Tetracetyl- α -methylglucoside*, obtained by the acetylation of E. Fischer's α -methylglucoside (Abstr., 1895, i, 438), melts at 101° , and has $[\alpha]_D + 175.35'$ at 20° . *Tetracetyl- β -ethylglucoside* crystallises from alcohol in colourless prisms, melts at $106-107^\circ$, has $[\alpha]_D - 27.4'$ at 16.5° , and when hydrolysed with alkali yields β -ethylglucoside in the form of a syrup having $[\alpha]_D - 30.7'$ at 20° , which is readily decomposed by emulsin, but not by yeast enzymes.

Acetonitroglucose (tetracetyldextrose nitrate), melting at $150-151^\circ$ (Colley 145°), may be obtained by the action of a solution of fuming nitric acid in chloroform on the bromo-compound or on the pentacetyldextrose melting at $130-131^\circ$, but not on the pentacetyl compound melting at 112° (Erwig and Koenigs, Abstr., 1889, 952). The nitro-compound is readily soluble in most organic solvents, with the exception of light petroleum, and has $[\alpha]_D + 149.19'$ at 18° ; it reduces boiling Fehling's solution, and when dissolved in glacial acetic acid gives a red coloration with brucine. When heated with dry sodium acetate and acetic anhydride, it is reconverted into the pentacetyldextrose. When warmed with methyl alcohol and either pyridine or barium carbonate, it yields tetracetyl- β -methylglucoside.

Acetonitrogalactose (*tetracetylgalactose nitrate*), $\text{NO}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_7\text{O}(\text{OAc})_4$, obtained from Erwig and Koenig's pentacetyl galactose, melts at $93-94^\circ$, and has $[\alpha]_D + 153.13'$ at 20° . When warmed with methyl alcohol and barium carbonate, it yields *tetracetyl- β -methylgalactoside*, which melts at $93-94^\circ$, and has $[\alpha]_D - 25.28'$ at 17° ; this does not reduce Fehling's solution, and does not give the brucine test.

J. J. S.

Cellose, a Biose from Cellulose. By ZDENKO H. SKRAUP and J. KÖNIG (*Ber.*, 1901, 34, 1115-1118).—The acetyl derivative obtained by the action of acetic anhydride and concentrated sulphuric acid, and regarded as a monose derivative owing to the results of molecular weight determinations being in correspondence with a pentacetylhexose (See Skraup, Abstr., 1899, i, 852), is now shown to be a biose, and the name *cellose* is given to it. In freezing phenol, the acetyl

compound has the mean molecular weight 546, in freezing acetic acid 572, whilst boiling point measurements give the numbers 663, 640 and 666 for the solvents benzene, chloroform, and ethyl acetate respectively; the value for an octacetylbirose is 678. On treating the acetate with concentrated alcoholic alkali hydroxide, the cellulose is obtained, and after repeated crystallisation from dilute alcohol, it forms a fine, snow-white powder consisting of microscopic, irregular prisms or plates, which retain $\frac{1}{4}\text{H}_2\text{O}$ when dried in a vacuum, but become anhydrous and faintly yellow on heating at 100° . The new sugar has not a characteristic taste, the after taste being faintly sweet. Its aqueous solution rapidly reduces Fehling's solution, but is only slightly, if at all, fermented by yeast. It shows distinct birotation and has $[\alpha]_D + 33.7^\circ$ in a 9.4766 per cent. solution at 20° . When hydrolysed, cellulose yields dextrose and possibly another sugar.

Just in the same way as maltose is the simplest polysaccharide obtained from starch, so is cellulose the simplest from cellulose. Cellulose and starch are hence fundamentally different substances, and the former cannot be regarded as a highly polymerised form of the latter. That it is improbable that any intramolecular rearrangement occurs when octacetylcellulose is hydrolysed with alcoholic alkali hydroxide is shown by submitting the α - and β -acetyl compounds of dextrose to the same treatment, the product in each case consisting almost entirely of dextrose.

T. H. P.

Molecular Weight of Glycogen. By HENRY JACKSON (*Proc. Camb. Phil. Soc.*, 1901, 11, 115—116).—A sample of glycogen was very carefully purified, in particular from inorganic salts, and was then found to lower the freezing point of water by an amount corresponding with a molecular weight of 9500—10000.

C. F. B.

Estimation of Pentosans by the Hydrochloric Acid Phloroglucinol Method. By E. KRÖBER (*J. Landw.*, 1901, 49, 7—20. Compare this vol., ii, 288).—The dry matter of different woods was found to contain the following amounts of pentosans: fir, 11.62; beech, 25.91 (= 23.58 per cent. of xylan); and guaiac 18.16 per cent. (compare Counciler, *Chem. Zeit.*, 1894, 966, and *Mündener Forstl. Hefte.*, 11, 21, and 12, 79; Flint, *Inaug. Diss. Göttingen*, 1892).

Dry wood gum, free from ash, from beech wood and wheat straw yielded 82.3 to 88.1 per cent. of xylan (compare Rimbach, *Diss. Göttingen*, 1898).

Determinations of pentosans were made in "crude fibre" prepared by Henneberg's method, by König's method (boiling with glycerol-sulphuric acid, *Zeit. Unters. Nahr.-und Genussmittel*, 1898, 3), and by Lebbin's hydrogen peroxide method (*Arch. Hyg.*, 28, 212). The "crude fibre" from meadow hay and from wheat meal prepared by Henneberg's method yielded 3.97—4.29 and 0.24—0.25 per cent. of pentosans. Lower results were obtained with "crude fibre" prepared by König's method (from rye straw, wheat bran, wheat meal, hay, and cotton seed meal), the percentages of pentosans being 0.25 to 0.80). Lebbin's process yielded "crude fibre" from rye straw containing 26.98—27.00 per cent. of pentosans.

Cotton-wool yielded 0.61 per cent. of furfuraldehyde; oxycellulose

prepared from the same cotton-wool yielded 1.86, 0.69, and 1.42 per cent. ; whilst a calcium salt from oxycellulose yielded 3.24 per cent. of furfuraldehyde (compare Gans, *Diss. Göttingen* ; Rimbach, *loc. cit.* ; Sestini, *L'Orosi*, 1898 ; and Suringar, *Diss. Göttingen*, 1896).

Determinations of water, ash, and pentosans were made in papers employed for newspapers in Germany, Holland, and Canada. From the results obtained, estimations are made of the probable percentages of wood and of sulphite-cellulose in the paper. A number of samples of writing and other papers were also examined. All the papers contained more than 5 per cent. of pentosans (in dry substance free from ash) and most contained more than 10 per cent. ; in one case, as much as 12.9 per cent. was found.

N. H. J. M.

Behaviour of Aqueous Formaldehyde towards Gun-cotton. By LUDWIG VANINO (*Ber.*, 1901, 34, 1128).—When gun cotton is moistened with a 20 per cent. aqueous solution of formaldehyde and then allowed to dry, either at the ordinary temperature or on the water-bath, it loses its capacity of exploding by percussion, without apparently being decomposed. If the paraformaldehyde is removed from the gun-cotton either by boiling with water or by heating the cotton, it is found that the original explosibility is regained.

T. H. P.

New Base Derived from Glucose. By LÉON MAQUENNE and E. ROUX (*Compt. rend.*, 1901, 132, 980—983. Compare Fischer, *Abstr.*, 1887, 567).—*Glucamine*, $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_4\cdot\text{CH}_2\cdot\text{NH}_2$, is produced by reducing dextroseoxime in a cold 10 per cent. aqueous solution with 3 per cent. sodium amalgam, sulphuric acid being slowly added during the reaction in order to neutralise the sodium hydroxide produced. It is isolated by means of its *neutral oxalate*, $2\text{C}_6\text{H}_{15}\text{NO}_5\cdot\text{H}_2\text{C}_2\text{O}_4$, a substance crystallising from dilute alcohol in glistening, hexagonal plates. The base itself, obtained as a mass of ill-defined crystals by treating the oxalate with an equivalent amount of calcium hydroxide, melts at 127—128°, is soluble in water and alcohol, but not in ether. In a 10 per cent. aqueous solution it has $[\alpha]_D - 8^\circ$ and does not exhibit mutarotation.

The base has a sweet and caustic taste, it absorbs carbon dioxide and yields salts which are all soluble in water but not in alcohol, the latter solvent precipitating them from their aqueous solutions in a syrupy condition. The yellow picrate is amorphous and the platinum-chloride crystallises with difficulty.

An *oxamide* having the composition $\text{C}_{14}\text{H}_{28}\text{O}_{12}\text{N}_2$, and $[\alpha]_D - 15.3^\circ$ is obtained by heating the oxalate at 180°.

Glucamine does not reduce Fehling's solution, and behaves like ammonia in precipitating the hydroxides from solutions of the metallic salts ; ferric hydroxide, however, redissolves, yielding a brown solution ; with copper sulphate, it yields a blue solution which deposits small, blue crystals ; mercuric chloride and silver nitrate give white precipitates, that derived from the latter reagent giving rise to a mirror on warming. Glucamine gives the iodoform reaction on boiling with iodine solution ; it is only slowly attacked by nitrous acid in the cold, at higher temperatures, however, the reaction is more rapid, and a mixture

of levorotatory reducing sugars is produced which yields glucosazone on treatment with phenylhydrazine acetate. Towards ethyl oxalate, benzaldehyde, acetylacetone, and potassium cyanate, glucamine behaves as a primary base and yields crystallisable products with these reagents. The absence of mutarotation shows that the geometrical configuration of the base is stable in aqueous solution; in this respect the compound resembles the hexatomic polyhydric alcohols and differs from chitosamine which contains a carbonyl group. G. T. M.

Action of Reducing Gases on Thiocyanates. By JAMES T. CONROY, OLIVER HESLOP, and J. B. SHORES (*J. Soc. Chem. Ind.*, 1901, 20, 320—322).—On passing dry hydrogen through molten potassium thiocyanate previously dried at 100° and heated at 600° , decomposition is complete after $2\frac{1}{2}$ hours. Calculated in terms of the percentage of thiocyanate decomposed, the product contains potassium cyanide 71, hydrogen sulphide 71, hydrogen cyanide 18, potassium sulphide 24, and ammonia 6.5, showing that decomposition occurs principally according to the equation $\text{KCNS} + \text{H}_2 = \text{H}_2\text{S} + \text{KCN}$, and partially thus, $2\text{KCN} + \text{H}_2\text{S} = \text{K}_2\text{S} + 2\text{HCN}$ (compare Sestini and Funaro, *Abstr.*, 1882, 1180, and Playfair, *J. Soc. Chem. Ind.*, 1892, 11, 14). Ninety-six per cent. of the total nitrogen is thus accounted for, and 95 per cent. of the total sulphur; the origin of the ammonia is uncertain, but is probably due to water being present. Conversely, when dry hydrogen sulphide is passed into fused potassium cyanide at a dull red heat, hydrogen cyanide is evolved, but two-thirds of the cyanide is converted into thiocyanate, owing probably to the hydrogen sulphide initially dissociating into hydrogen and sulphur.

With sodium thiocyanate, hydrogen yields much less metallic cyanide and hydrogen sulphide than with the potassium salt, more ammonia and more of the metallic sulphide being formed. Calcium thiocyanate yields only traces of hydrogen cyanide and sulphide, white fumes being evolved which are not soluble in dilute acid or alkali. The product remaining consists entirely of calcium sulphide. With barium and copper thiocyanates, the metallic sulphides only are formed, hydrogen cyanide and hydrogen sulphide being evolved along with other volatile products. W. A. D.

The Benzene Problem from the Stereochemical Standpoint. By EMIL ERLÉNMEYER, jun. (*Annalen*, 1901, 316, 57—71).—A discussion of the molecular configuration of benzene, illustrated by diagrams of space formulæ not suitable for abstraction. G. T. M.

The Closer Coalescence of the Multivalent Atoms of Molecular Systems containing Neighbouring Double-linkings. By EMIL ERLÉNMEYER, jun. (*Annalen*, 1901, 316, 71—74).—The formation of ringed systems of the benzene type illustrates the tendency which the carbon atoms of unsaturated compounds possess of becoming interlinked to the maximum extent. Assuming that this tendency is general, a ready explanation is furnished of the behaviour of compounds containing the residue $-\text{C}:\text{C}:\text{C}:\text{C}-$ towards reducing agents; this configuration changes to that of the closed chain system, $\begin{array}{c} \text{C}:\text{C} \\ | \quad | \\ \text{C}:\text{C} \end{array}$, and

the hydrogen atoms become attached to the carbon atoms which were originally at the end of the open chain. This assumption renders the hypothesis of partial valency superfluous (compare Thiele, Abstr., 1899, i, 554, and Knoevenagel, Abstr., 1900, ii, 534) and readily explains the reduction of benzil and the formation of *d*- and *l*-isohydrobenzoin and hydrobenzoin from benzaldehyde.

G. T. M.

4-Hydroxyhydrindene. New Derivatives of Xylene and Ethylbenzene. By J. MOSCHNER (*Ber.*, 1901, 34, 1257—1262. Compare Abstr., 1900, i, 344).—Hydrindene-4-sulphonic acid was found in the liquors obtained on sulphonating ψ -cumene, and its constitution determined by oxidation to a sulphophthalic acid which gave 3-hydroxyphthalic acid when fused with potassium hydroxide.

4-Hydroxyhydrindene, prepared by fusing the sulphonic acid with potassium or sodium hydroxide, is an oil which boils at 244—246°, does not solidify on cooling, and has an odour resembling that of phenol. *4-Methoxyhydrindene* is an aromatic oil boiling at 225—227°.

1:3-Xylene-5-sulphinic acid, prepared by Gattermann's method from *s-m*-xylidine, melts at 75—76°, or 2° lower than the 1:3:4-acid (Gattermann, Abstr., 1899, i, 517).

1:3-Xylene-5-sulphonic chloride crystallises from ether and melts at 89—90°. The *sulphonamide* crystallises from hot water in needles and melts at 135°.

1:2-Xylene-3-sulphinic acid melts at 105°, and on oxidation forms the 1:2:3-sulphonic acid.

The melting points of the sulphonamides of this series are 60—63° higher than those of the sulphonic acids in each of the five cases where data are available.

Ethyl-4-anisole is an aromatic liquid which boils at 199—200°, and when oxidised yields *p*-methoxybenzoic acid. *Ethyl-4-phenetole* boils at 211° and not at 200° (Errera, Abstr., 1885, 775).

T. M. L.

Action of Ethylidene Chloride and Methylene Chloride on Naphthalene in Presence of Aluminium Chloride. By F. BODROUX (*Bull. Soc. Chim.*, 1901, [iii], 25, 491—497).—The action of ethylidene chloride on naphthalene in the presence of aluminium chloride results in the production of β -methylnaphthalene together with small quantities of α -methylnaphthalene, α - and β -ethylnaphthalenes, dimethylnaphthalenes, and $\beta\beta$ -dinaphthyl; a large quantity of methane is also evolved. The principal products of the action of methylene chloride on naphthalene are β -methylnaphthalene and $\beta\beta$ -dinaphthyl. Full details of the separation and identification of these products are given in the paper.

N. L.

Triphenylchloromethane. By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1901, 23, 109—110).—A polemical reply to Norris and Sanders (Abstr., 1901, i, 198).

E. G.

Tritolylchloromethane. By MOSES GOMBERG and O. W. VOEDISCH (*J. Amer. Chem. Soc.*, 1901, 23, 177—178).—*Tritolylchloromethane* may be obtained by the action of aluminium chloride on a mixture of carbon tetrachloride and toluene, the method employed being that

previously described for the preparation of the corresponding triphenyl-compound (Gomberg, Abstr., 1901, i, 77). When boiled with alcohol, it yields the *ethoxy*-derivative melting at 105°, and if boiled with water, the *carbinol* is produced. E. G.

Oxidation of Aniline. By ERNST BÖRNSTEIN (*Ber.*, 1901, 34, 1268—1274).—When dioxide of lead or manganese is added gradually to a neutral aqueous solution of aniline hydrochloride or sulphate, azophenine melting at 246° and aminoquinonediphenylimide are produced together with some azobenzene.

Aminoquinonediphenylimide, $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NPh})_2$, crystallises in stellate groups of dull red prisms with a faintly bluish tint, melts at 167°, and is readily soluble in most organic solvents but only sparingly in methyl or ethyl alcohol. It dissolves in concentrated sulphuric acid to form a red solution which becomes blue when heated, and on dilution yields a blue solution with a red fluorescence. It is decomposed by dilute mineral acids and also by acetic acid. When reduced with alcoholic ammonium sulphide and the product distilled under reduced pressure in an atmosphere of coal gas, a residue is obtained which yields a *substance*, $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NPh})_2$, crystallising in aggregates of lustrous needles and melting at 83°; its *acetyl* derivative, $\text{NHAc} \cdot \text{C}_6\text{H}_3(\text{NPh})_2$, crystallises in colourless, six-sided plates, melts at 170—171°, and dissolves readily in alcohol, ethyl acetate, benzene, acetone, or chloroform.

When aminoquinonediphenylimide is heated with aniline in presence of aniline hydrochloride or zinc chloride, it is converted into azophenine. E. G.

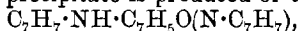
Aniline and Quinoline Derivatives of Metallic Trichlorides. By HUGO SCHIFF (*Ber.*, 1901, 34, 804—805).—Some of the compounds described by Vanino and Hauser (Abstr., 1900, i, 641; this vol., i, 289) were prepared long ago by the author. The chloride and the base were made to unite in benzene solution by the aid of heat; from dilute hydrochloric acid they sometimes crystallised with HCl (and H_2O). The compounds cited are $\text{BiCl}_3 \cdot 3(\text{NH}_2\text{Ph}, \text{HCl}) \cdot 3\text{H}_2\text{O}$; $\text{BiCl}_3 \cdot 3(\text{NH}_2\text{Ph}, \text{HCl})$; $\text{BiCl}_3 \cdot 3(\text{C}_6\text{H}_7\text{N}, \text{HCl})$; $\text{SbCl}_3 \cdot 3\text{NH}_2\text{Ph}$, melting at 80°; $\text{SbCl}_3 \cdot 3(\text{NH}_2\text{Ph}, \text{HCl}) \cdot 3\text{H}_2\text{O}$; $\text{SbI}_3 \cdot 3(\text{NH}_2\text{Ph})$. C. F. B.

Oxidation of *p*-Toluidine. By ERNST BÖRNSTEIN (*Ber.*, 1901, 34, 1274—1284).—By the action of potassium dichromate on *p*-toluidine sulphate, Perkin (*Trans.*, 1880, 37, 546) obtained two compounds which he regarded as tri-*p*-tolylene-triamine and tolyl-tri-*p*-tolylene-triamine; the former substance, which had been previously obtained by Barsilowski (Abstr., 1873, 273) was shown by Green (*Trans.*, 1893, 63, 1395) to be amino-*p*-toluoquinoneditylimide. The same two compounds have been obtained by the author by the action of lead dioxide on a neutral solution of *p*-toluidine hydrochloride or sulphate, *p*-ditolylamine and small quantities of *p*-azotoluene being simultaneously produced, whilst the employment of manganese dioxide under certain conditions resulted in the formation of aminotoluoquinoneditylimide and azotoluene.

Amino-*p*-toluoquinoneditylimide melts at 235°. When heated

with a mixture of *p*-toluidine, *p*-toluidine hydrochloride, and alcohol, it yields the *hydrochloride* of a base, crystallising in yellow plates and melting at 282° ; the *base* itself, $\text{NH}_2 \cdot \text{C}_7\text{H}_3(\text{N} \cdot \text{C}_7\text{H}_7)_2(\text{NH} \cdot \text{C}_7\text{H}_7)_2$, crystallises from alcohol in orange-red leaflets and melts at $250-251^{\circ}$. The formation of the hydrochloride is accompanied by that of another *substance* which forms yellowish-red crystals and melts at $321-322^{\circ}$.

p-Toluidino-*p*-toluquinoneditolyimide, $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{C}_7\text{H}_5(\text{N} \cdot \text{C}_7\text{H}_7)_2$, identical with the second substance described by Perkin (*loc. cit.*), melts at 183° ; if it is dissolved in alcoholic sulphuric acid (5 per cent.), left for 24 hours, and then saturated with ammonia, on dilution with water a precipitate is produced of a *base*,



which crystallises from hot alcohol in lustrous, dark reddish-brown needles, melts at 181° , and dissolves readily in benzene, toluene, chloroform, acetone, or ether; small quantities of another *compound* are simultaneously formed, which is obtained in tabular, red crystals with a bluish tint. The former substance yields a well-crystallised *hydrochloride*, *sulphate*, and *platinichloride*; if it is dissolved in concentrated sulphuric acid, a green solution is obtained, which on dilution with water forms an orange-yellow solution containing the sulphate of a new, yellow, crystalline *base*. E. G.

[Action of Cyanogen Bromide on Dimethylaniline]. By ROLAND SCHOLL and WILHELM NÖRR (*Ber.*, 1901, **34**, 1345).—Methylcyanoaniline (phenylmethylecyanamide), described by the authors as a new substance (Abstr., 1900, i, 435), has previously been prepared by Wallach (Abstr., 1899, i, 659) and by Stieglitz and MacKee (Abstr., 1900, i, 340). K. J. P. O.

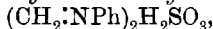
Substituted Ammonium Compounds of the Type $\text{NR}'\text{R}''\text{R}'''_2\text{X}$. By HUMPHRY O. JONES (*Proc. Camb. Phil. Soc.*, 1901, **11**, 111—114).—Phenylbenzyl dimethylammonium iodide is formed from dimethylaniline and benzyl iodide, or, better, from benzylmethylaniline and methyl iodide; the same product is obtained in both cases, even at 0° . It melts at $163-164^{\circ}$; the corresponding *d-camphorsulphonate* obtained from it by treatment with silver camphorsulphonate and moist ethyl acetate, melts and decomposes at 189° .

Phenyl dibenzyl methylammonium iodide is formed from benzylmethylaniline and benzyl iodide, and melts at $134-135^{\circ}$; the *chloride*, obtained from it by double decomposition with silver chloride, melts at $160-161^{\circ}$; the *d-camphorsulphonate* melts at $135-138^{\circ}$ and crystallises with 1CHCl_3 ; the *d-bromocamphorsulphonate* was not obtained crystalline. The chloride cannot be obtained from benzylmethylaniline and benzyl chloride, either at the ordinary temperature or at 100° , and the iodide cannot be prepared from dibenzylaniline and methyl iodide; at 100° , phenyltrimethylammonium iodide is obtained instead. C. F. B.

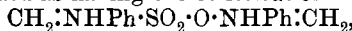
Study of Aldehydes: Compounds of Schiff's Bases with Sulphurous Acid and the Alkali Hydrogen Sulphites. By ALEXANDER EIBNER (*Annalen*, 1901, **316**, 89—143).—Ethylideneaniline hydrogen sulphite, $\text{NPh} \cdot \text{CHMe} \cdot \text{H}_2\text{SO}_3$, prepared either by adding acetaldehyde to a solution of aniline in excess of sulphurous acid

or by shaking ethylideneaniline with a solution of this acid, crystallises in colourless, prismatic needles melting at 94° ; it can be crystallised from alcohol without alteration, but decomposes in contact with water or aqueous solutions of ammonia and sodium hydroxide, regenerating the ethylidene base. *Ethylideneaniline sodium sulphite*, formed either by treating the preceding compound with sodium carbonate solution or by adding aniline to the sodium hydrogen sulphite compound of acetaldehyde dissolved in water, crystallises in snow-white, lustrous leaflets; it readily dissolves in water, yielding a neutral solution from which the hydrogen sulphite compound is precipitated by the cautious addition of dilute hydrochloric acid. These reactions indicate that these compounds are constituted on the type of sulphonates having respectively constitutions represented by the following formulæ, $\text{SO}_2 \langle \text{CHMe} \rangle \text{NH}_2\text{Ph}$ and $\text{ONa} \cdot \text{SO}_2 \cdot \text{CHMe} \cdot \text{NHPh}$.

Neutral anhydroformaldehyde aniline hydrogen sulphite,

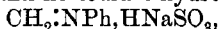


obtained by adding formaldehyde solution to an aqueous sulphurous acid solution of aniline containing excess of the base, crystallises in snow-white leaflets and decomposes at $129\text{--}130^{\circ}$; it gradually changes into a yellow, amorphous, insoluble substance which does not regenerate the aldehyde on heating with dilute sulphuric acid; the original compound is regarded as having the constitution



whilst the product of transformation is in all probability a derivative of diphenylmethane.

Anhydroformaldehydeaniline sodium hydrogen sulphite,



obtained by Hofer from anhydroformaldehydeaniline, may also be prepared by slowly adding aniline to a sulphurous acid solution of formaldehyde and gently heating the mixture on the water-bath.

Neutral propylidenedianiline hydrogen sulphite,



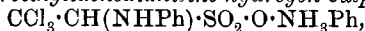
produced by shaking together propaldehyde and a sulphurous acid solution of aniline containing excess of the base, crystallises in snow-white prisms and decomposes at 89° .

Propylideneaniline sodium hydrogen sulphite, $\text{CH}_2\text{Me} \cdot \text{CH} \cdot \text{NPh} \cdot \text{H}_2\text{SO}_3$, prepared by adding aniline to a solution of propaldehyde in sulphurous acid, crystallises from the mixture, after concentration under diminished pressure, in silky, slender needles; it is readily decomposed on boiling with water.

Trichloroethylideneaniline hydrogen sulphite, $\text{CCl}_3 \cdot \text{CH} \langle \text{NH}_2\text{Ph} \rangle \text{SO}_2 \text{O}$,

results from the interaction of aniline dissolved in excess of sulphurous acid and chloral or freshly prepared solutions of the aldehyde; it separates in thin, monoclinic plates and melts at 93° . The compound may be crystallised from hot water without alteration, but is instantly decomposed by sodium carbonate solution and becomes yellow on exposure to the air (compare Boessneck, Abstr., 1888, 942).

Hydrated trichloroethylidenedianiline hydrogen sulphite,



slowly separates from an aqueous solution containing aniline, chloral hydrate, and excess of sulphurous acid; it can be crystallised from water and is perfectly stable in the atmosphere; it forms long needles melting at 165° and dissolves in sodium carbonate solution without decomposition.

i-Butylidenedianiline anhydrosulphite, $C_3H_7 \cdot CH(NHPh)_2 \cdot SO_2$, obtained either by adding *i*-butaldehyde to an aniline solution in excess of sulphurous acid or by treating the hydrogen sulphite compound of *i*-butaldehyde with aniline, crystallises in sparingly soluble, white needles and melts at $126-127^{\circ}$.

i-Valerylidenedianiline anhydrosulphite, $C_4H_9 \cdot CH(NHPh)_2 \cdot SO_2$, prepared like the preceding compounds in aqueous solutions and also by passing sulphur dioxide into an ethereal solution of *i*-valerylidene-aniline dissolved in ether, separates as a crystalline powder melting at $128-129^{\circ}$.

Heptylidenedianiline anhydrosulphite is obtained in small needles which obstinately retain the last traces of moisture, and when perfectly dry melt at $107-108^{\circ}$. The compound can be crystallised from water or alcohol, but is decomposed with its generators by sodium carbonate solution. The aniline anhydro-base of valeraldehyde and cenanthaldehyde do not combine with sodium hydrogen sulphite; on the other hand, the sodium hydrogen sulphite derivatives of these aldehydes are decomposed by aniline, yielding the corresponding anhydrosulphites.

Benzylidenedianiline anhydrosulphite, $CHPh(NHPh)_2 \cdot SO_2$ (compare Michaelis, Abstr., 1891, 716), produced either by adding benzaldehyde to a strongly acid solution of aniline in sulphurous acid or by passing sulphur dioxide into a solution of benzylideneaniline in dry ether, crystallises in aggregates of needles and melts at 125° ; it is immediately decomposed by sodium carbonate solution, and when heated with water changes into a compound, $C_{10}H_{18}N_2 \cdot SO_2 \cdot \frac{1}{2}H_2O$, which crystallises in flattened needles and melts and decomposes at $132-135^{\circ}$.

m-Nitrobenzylidenedianiline anhydrosulphite,
 $NO_2 \cdot C_6H_4 \cdot CH(NHPh)_2 \cdot SO_2$,

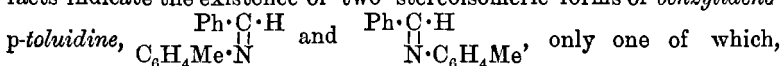
and *m*-nitrobenzylidenedianiline hydrogen sulphite,
 $NO_2 \cdot C_6H_4 \cdot CH : NPh, H_2SO_3$,

are produced simultaneously by adding an alcoholic solution of *m*-nitrobenzaldehyde to aniline dissolved in sulphurous acid; the former is soluble in alcohol and crystallises in yellow needles and melts at 128° , the latter is insoluble in alcohol and crystallises from water in colourless leaflets melting at 177° . The yellow compound, when dissolved in alcohol and treated with sulphurous acid, is converted into the white sulphite, the converse change being effected by the action of heat on the latter substance. The compound, $OH \cdot C_6H_4 \cdot CH : NPh, H_2SO_3$, melts at 128° , and is formed by adding salicylaldehyde to an aqueous aniline sulphite solution; it is decomposed by sodium carbonate and also by hot water or alcohol.

G. T. M.

Condensation Products of Aldehydes and Amines. By ARTHUR HANTZSCH and OTTO SCHWAB (*Ber.*, 1901, 34, 822-839).—When *p*-toluidine is warmed with benzaldehyde (1 mol.), a yellowish oil

is obtained which, after cooling, may behave in four different ways. (1) It rapidly forms a crystalline mass melting at 35° ; (2) it partially solidifies, the crystals, after being drained, melting below 35° ; the residual oil only deposits crystals after several days, and these melt between 28° and 33° ; (3) the product remains liquid at the ordinary temperature, even after the addition of a crystal of the substance melting at 35° ; when cooled, it solidifies at 11° to a mass melting at 12.5° , but after several days it deposits crystals melting at 35° , and after several months becomes completely solid and then melts at 35° ; (4) the product is liquid at the ordinary temperature, but very gradually solidifies on adding a crystal of the compound melting at 35° . These facts indicate the existence of two stereoisomeric forms of *benzylidene-p-toluidine*,



that melting at 35° , is stable; when this form is heated at the melting temperature for several minutes, it melts, after solidification, at temperatures varying between 12° and 33° . The original melting point is, however, regained when the solidified product is kept for some time at the ordinary temperature.

Benzylideneaniline shows a somewhat similar behaviour; it melts at 48° , and after solidifying remelts at 54° , whilst very varying melting points are attributed to it by other authors. The following compounds apparently exist in only one form; the melting points are given in brackets. *p-Chlorobenzylideneaniline*, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH} \cdot \text{NPh}$, white scales (66°); *p-chlorobenzylidene-p-chloroaniline*, yellowish-white needles (111°); *o-chlorobenzylidene-p-chloroaniline*, white crystals (68°); *m-nitrobenzylidene-p-chloroaniline*, yellowish crystals (81°); the *hydrochloride* melting at 185° ; *p-nitrobenzylidene-p-chloroaniline*, yellow needles (128°); *benzylidene-p-anisidine*, white leaflets (142°); *o-hydroxybenzylidene-p-bromoaniline*, lustrous, yellow leaflets (112°); *p-methoxybenzylidene-p-anisidine*, white, lustrous leaflets (142°).

Benzylidene-p-chloroaniline, $\text{CHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Cl}$, crystallises from alcohol in beautiful, white leaflets, melts at 62° , and yields a white, crystalline *hydrochloride*; this melts and decomposes at 194° , is converted by moist air into benzaldehyde and *p-chloroaniline hydrochloride*, and, with aqueous sodium carbonate below 0° yields *benzaldehyde-p-chloroaniline*, $\text{OH} \cdot \text{CHPh} \cdot \text{C}_6\text{H}_4\text{Cl}$, which melts at about 120° when rapidly heated, and is thereby converted, with loss of $1\text{H}_2\text{O}$, into *benzylidene-p-chloroaniline*. *Benzylidene-p-bromoaniline* crystallises from alcohol in white leaflets, melts at 67° , and yields a *hydrochloride* melting and decomposing at 195° ; *benzaldehyde-p-bromoaniline*, $\text{OH} \cdot \text{CHPh} \cdot \text{C}_6\text{H}_4\text{Br}$, melts at about 120° , loses $1\text{H}_2\text{O}$, and subsequently melts at 67° . The *hydrochlorides* of the following compounds, when decomposed by aqueous sodium carbonate, regenerate their bases. 2 : 4 : 6-*Trimethylbenzylideneaniline* melts at 56° , and 2 : 4 : 6-*trimethylbenzylidene-p-cumidine* at 82° (the *hydrochloride* decomposes at 212°); 2 : 4 : 6-*trimethylbenzylidene-p-chloroaniline* crystallises from alcohol in long needles, the yellow *hydrochloride* decomposing at 183° . *o-Hydroxybenzylideneaniline* forms yellow crystals and melts at 51° .

Benzaldehyde and *p-nitroaniline*, after long heating at 120° , yield *benzylidene-p-nitroaniline* melting at 118° , but at the ordinary tempera-

ture, in absolute alcoholic ethereal solution, 2 mols. of the base combine with 1 mol. of the aldehyde to form *benzylidenebis-p-nitroaniline*, $\text{CHPh}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, which, obtained in an impure state, was considered by von Miller and Rohde (Abstr., 1892, 1189) to be the compound $\text{OH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$; it forms yellow crystals, melts at 85° , and is decomposed by heating, either alone or with benzene or water, into benzylidene-*p*-nitroaniline and *p*-nitroaniline.

Benzylidenebisaminothiazole, $\text{CHPh}(\text{C}_8\text{H}_3\text{N}_2\text{S})_2$, obtained from benzaldehyde and aminothiazole (2 mols.), melts indefinitely when slowly heated, but instantaneously when plunged into a bath heated to 138° ; decomposition here occurs into benzylideneaminothiazole and aminothiazole, but recombination occurs on cooling (compare Hantzsch and Witz, this vol., i, 401).

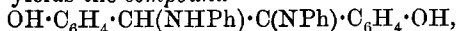
Benzylidene-*p*-toluidine combines with methyl iodide at the ordinary temperature to form the crystalline *methiodide*, $\text{CHPh}\cdot\text{NMeI}\cdot\text{C}_6\text{H}_4\text{Me}$, which is decomposed by water or moist air, yielding benzaldehyde, and by aqueous sodium hydroxide yielding *p*-toluidine, not methyl-*p*-toluidine. *Benzylidene-p-toluidine ethiodide* melts and decomposes at 170° ; the methiodide and ethiodide of benzylideneaniline are crystalline, but rapidly decompose, yielding complex products; the existence of Borodin's bases of the type $\text{CHPh}\cdot\text{NPhMe}\cdot\text{OH}$ seems doubtful (compare *Annalen*, 1859, 111, 254).

Ethylidenebenzylamine, from acetaldehyde and benzylamine, boils at 145° and resinifies with methyl iodide; benzylidene-ethylamine (b. p. $187\text{--}188^\circ$) similarly does not yield a methiodide.

[Supplement by PAUL JACOBSON and A. STEINBRECK (compare *Diss., Heidelberg*, 1896)].—*o*-Hydroxybenzylidene-*o*-toluidine crystallises from light petroleum in needles, melts at $47\text{--}48^\circ$, and yields with iodine an unstable, violet, additive compound, $\text{C}_{14}\text{H}_{13}\text{ONI}_4$. *o*-Hydroxybenzylidene-*o*-bromoaniline forms yellow prisms melting at $85\text{--}86^\circ$. *Benzylidene-o-phenetidine* boils at $215\text{--}216^\circ$ under 20 mm. pressure; *o*-hydroxybenzylidene-*o*-phenetidine boils at $228\text{--}229^\circ$ under 17 mm. pressure.

W. A. D.

Condensation of *o*-Hydroxybenzylideneaniline. By OTTO SCHWAB (*Ber.*, 1901, 34, 839—840).—Although benzylideneaniline fails to undergo the benzoin condensation with potassium cyanide (von Miller and Plöchl, *Ber.*, 1896, 1730, and 1898, 2699), *o*-hydroxybenzylideneaniline readily yields the compound



at the ordinary temperature; it separates from alcohol in lustrous, yellow crystals and melts at 155° .

W. A. D.

Preparation of Morpholine. By WILHELM MARCKWALD and M. CHAIN (*Ber.*, 1901, 34, 1157—1159. Compare Knorr, Abstr., 1898, i, 601; 1899, i, 784).—*p*-Tolylsulphonedi- β -naphthoxyethylamide, $\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{N}(\text{CH}_2\cdot\text{O}\cdot\text{C}_{10}\text{H}_7)_2$, obtained from *p*-tolylsulphonamide (1 mol.), β -naphthyl bromoethyl ether (2 mols.), and alcoholic potash, crystallises from acetic acid, melts at 130° , and is only sparingly soluble in alcohol. When hydrolysed with mineral acids at $170\text{--}180^\circ$, it is quantitatively converted into toluene, sulphuric acid, β -naphthol, and morpholine.

Contrary to Weddige's statement (Abstr., 1881, 1137), a considerable amount of primary base, phenoxyethylamine, is obtained by the action of ammonia on phenyl bromoethyl ether (bromophenetole). The *hydrobromide* melts at 192—193°.

J. J. S.

Chloro-derivatives of *s*-Diphenylcarbamide and their Reactions. By FREDERICK D. CHATTAWAY and KENNEDY J. P. ORTON (*Ber.*, 1901, 34, 1073—1078).—*s*-Diphenylcarbamide is converted by hypochlorous acid into a diphenyldichlorocarbamide, the imino-hydrogen atom being replaced by chlorine. This substance readily undergoes molecular change, producing *s*-di-*p*-chlorophenylcarbamide, which, in its turn, can be converted into a dichloroamino-derivative, which passes by intramolecular change into *s*-di-2:4-dichlorophenylcarbamide. This series of changes can again be repeated, the final product being *s*-di-2:4:6-trichlorophenyldichlorocarbamide.

s-Diphenyldichlorocarbamide, $\text{CO}(\text{NPhCl})_2$, is obtained by the action of alkaline potassium hypochlorite solution on diphenylcarbamide, and crystallises in large, colourless prisms, which, when rapidly heated, melt at 101—102°, forming a colourless liquid, which then becomes dark coloured and explodes. When it is heated in acetic acid solution, molecular change takes place, *s*-di-*p*-chlorophenylcarbamide being produced along with small amounts of two isomeric dichlorophenylcarbamides. The main product has previously been described by Beilstein and Kurbatoff (*Annalen*, 1875, 176, 46), and is best prepared by heating carbamide with *p* chloroaniline. When it is treated with bleaching powder and potassium hydrogen carbonate, it yields *s*-di-*p*-chlorophenylmonochlorocarbamide, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CO}\cdot\text{NCl}\cdot\text{C}_6\text{H}_4\text{Cl}$, which crystallises in bundles of needles, or in long, thin plates, which melt at about 132° when rapidly heated, but solidify again at a somewhat higher temperature. *s*-Di-*p*-chlorophenyldichlorocarbamide, $\text{CO}(\text{NCl}\cdot\text{C}_6\text{H}_4\text{Cl})_2$, is produced along with the foregoing compound when chlorophenylcarbamide is treated with bleaching powder and acetic acid, and forms short, colourless prisms, which melt and partially decompose at 171—173° when rapidly heated. On treatment with acetic acid at 100°, it partially decomposes and partially undergoes molecular change, producing *s*-di-2:4-dichlorophenylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{Cl}_2)_2$, which can also be prepared by heating carbamide with 2:4-dichloroaniline, and crystallises in thin, colourless needles melting at 273°, with partial decomposition when rapidly heated. When it is treated with chlorine in presence of acetic acid and potassium acetate, it yields *s*-di-2:4-dichlorophenyldichlorocarbamide, $\text{CO}(\text{NCl}\cdot\text{C}_6\text{H}_3\text{Cl}_2)_2$, which crystallises in strongly refractive prisms, and melts and partially decomposes at about 160° when rapidly heated. When heated with acetic acid, it yields *s*-di-2:4:6-trichlorophenylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_2\text{Cl}_3)_2$, which crystallises in very thin needles melting with decomposition at 320—325° when rapidly heated. Alcoholic ammonia produces carbamide and 2:4:6-trichloroaniline. Bleaching powder and acetic acid convert it into *s*-di-2:4:6-trichlorophenyldichlorocarbamide, $\text{CO}(\text{NCl}\cdot\text{C}_6\text{H}_2\text{Cl}_3)_2$, which crystallises

in strongly refractive, four-sided prisms terminated by dome faces, and melts and decomposes at about 190° when rapidly heated.

A. H.

Bromination of *s*-Diphenylcarbamide. By FREDERICK D. CHATTAWAY and KENNEDY J. P. ORTON (*Ber.*, 1901, **34**, 1078—1081. Compare preceding abstract).—Bromine acts on *s*-diphenylcarbamide in a similar manner to chlorine, but the intermediate products have not been isolated. *s*-Di-*p*-bromophenylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Br})_2$, is obtained by the direct action of bromine on the carbamide in presence of acetic acid and sodium acetate, and crystallises in thin prisms which melt and decompose at about 330° when rapidly heated. On heating with alcoholic ammonia, it yields *p*-bromoaniline and carbamide. The compound described under this name by Otto (*Ber.*, 1869, **2**, 408), and by Sarauw (*Ber.*, 1882, **15**, 42), is stated by them to sublime at 225° without previously melting.

s-Di-2 : 4-dibromophenylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{Br}_2)_2$, is obtained by boiling the carbamide with excess of bromine in presence of acetic acid and sodium acetate. It crystallises in colourless, silky needles, and melts and partially decomposes at 281° when rapidly heated. Alcoholic ammonia converts it into 2 : 4-dibromoaniline and carbamide.

s-Di-2 : 4 : 6-tribromophenylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_2\text{Br}_3)_2$, is obtained when a mixture of diphenylcarbamide, bromine, acetic acid, and sodium acetate is heated at 130—135°. It crystallises in colourless, hair-like needles, which melt and decompose at about 320°. Alcoholic ammonia converts it into carbamide and 2 : 4 : 6-tribromoaniline.

A. H.

Electrolysis of Phenol in presence of Hydrogen Haloids. By HERIBERT ZEHLANT (*Zeit. Elektrochem.*, 1901, **7**, 501—505).—In presence of hydrochloric acid, phenol is oxidised at the anode and not chlorinated, owing to the facts that oxygen is liberated at a lower potential than chlorine and that phenol acts as a depolariser for anodic oxygen. In presence of *N* hydrobromic acid, the same thing occurs, but when 4 *N* hydrobromic acid is used, from which bromine ions are discharged at a lower potential, a certain amount of brominated product is obtained. In presence of hydriodic acid, iodine is liberated without acting on the phenol.

T. E.

Some Derivatives of Phenyl Ether. By CARL HÄUSSERMANN and AUG. MÜLLER (*Ber.*, 1901, **34**, 1069. Compare Abstr., 1896, i, 533).—The potassium derivatives of the cresols react with *o*- and *p*-chloronitrobenzene in a similar manner to potassium phenoxide, whereas those of the naphthols under similar circumstances simply act as reducing agents. Quinol *p*-nitrodiphenyl ether, is obtained by heating the potassium compound of *p*-hydroxyphenyl ether with *p*-chloronitrobenzene, and crystallises in lustrous plates melting at 91—92.5°. On reduction in alcoholic solution with tin and hydrochloric acid, it yields quinol *p*-aminodiphenyl ether, which crystallises in almost colourless prisms melting at 83—84.5°. The hydrochloride is sparingly soluble in cold water and crystallises in silvery scales melting at 210°, whilst the sulphate is insoluble in boiling water. The base can be converted into a diazo-compound which yields reddish azo-compounds. When

the base is treated in alcoholic solution with nitrous acid and the liquid boiled, *quinol diphenyl ether* is produced, which crystallises in white needles melting at 74—75°, can be distilled at the ordinary pressure and is not affected by acetic anhydride. A. H.

Action of Iodine and Yellow Mercuric Oxide on Anethole, Estragole, Safrole, &c. By J. BOUGAULT (*Bull. Soc. Chim.*, 1901, [iii], 25, 444—446. Compare *Abstr.*, 1900, i, 494, 641).—The action of iodine and mercuric oxide on cyclic compounds containing a propenylic side chain takes place in two stages, the first stage consisting in the fixation of HIO with the formation of a compound, $R \cdot CHI \cdot CHMe \cdot OH$, which then undergoes transformation into the aldehyde, $R \cdot CHMe \cdot CHO$, with elimination of HI. These intermediate compounds may be isolated by employing a limited amount of mercuric oxide, or by replacing the latter by mercuric chloride; they are more or less unstable, uncrystallisable substances which are readily reduced by zinc and acetic acid and are decomposed on exposure to air and light with liberation of iodine. N. L.

New Synthesis of Aromatic Sulphones. By FRITZ ULLMANN and G. PASDERMAJIAN (*Ber.*, 1901, 34, 1150—1156).—Aromatic sulphinic acids readily react with alcoholic solutions of halogen derivatives of aromatic nitro-compounds, yielding diphenylsulphone derivatives. In certain cases, for example, with *o*- and *p*-chloronitrobenzene, chloronitrobenzoic acid, &c., it is necessary to work under increased pressure and in presence of sodium acetate.

2:4:6-*Trinitrodiphenylsulphone*, $C_6H_2(NO_2)_3 \cdot SO_2Ph$, crystallises in pale yellow, well developed rhombohedra melting at 233° (corr.), and insoluble in alcohol or ether. 2:4-*Dinitrodiphenylsulphone*, $C_6H_3(NO_2)_2 \cdot SO_2Ph$, crystallises in colourless needles, melts at 157°, and dissolves in hot benzene or acetic acid. When reduced with stannous chloride and hydrochloric acid in the presence of alcohol, it yields 2:4-*diaminodiphenylsulphone*, which crystallises in colourless, hexagonal needles melting at 188°, and insoluble in water or ether; the *diacetyl* derivative crystallises in needles melting at 197°. 2-*Nitrodiphenylsulphone*, $NO_2 \cdot C_6H_4 \cdot SO_2Ph$, crystallises in colourless, feathery needles melting at 147.5°, and readily soluble in most organic solvents. 2-*Aminodiphenylsulphone* crystallises in glistening plates melting at 122°, and yields an *acetyl* derivative melting at 132°. 2-*Hydroxydiphenylsulphone*, obtained from the amino-compound, crystallises in small, hexagonal prisms melting at 82°, and readily soluble in most organic solvents or in alkalis. A small amount of diphenylsulphone is also obtained as a by-product.

4-*Nitrodiphenylsulphone* crystallises in colourless needles melting at 143°, and readily soluble in benzene, alcohol, or acetic acid. 4-*Aminodiphenylsulphone* crystallises in needles melting at 176°, and yields an *acetyl* derivative crystallising in prisms and melting at 195°.

2:6-*Dinitrodiphenylsulphone-4-carboxylic acid*,
 $CO_2H \cdot C_6H_3(NO_2)_2 \cdot SO_2Ph$,
 crystallises from hot water in long, colourless needles which darken at 220° and decompose and melt at 240°.

2-*Nitrodiphenylsulphone-4-carboxylic acid* forms yellowish crystals

melting at 255—260°, and readily soluble in alcohol or acetic acid. 2-Aminodiphenylsulphone-4-carboxylic acid melts at 270—275°.

J. J. S.

So-called Dinaphthylene Glycol Anhydride. By ROBERT FOSSE (*Compt. rend.*, 1901, 132, 1127—1129. Compare this vol., i, 322).—The compound described by Rousseau (*Abstr.*, 1882, 1299) as the anhydride of dinaphthylene glycol is identical with dinaphthaxanthen.

C. H. B.

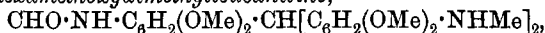
Derivatives of Eupittone [Hexamethoxyaurin]. By CARL LIEBERMANN and FRITZ WIEDERMANN (*Ber.*, 1901, 34, 1031—1040).—Eupittone is shown by Zeisel's method to contain six methoxy-groups. The *hydrochloride*, $C_{25}H_{26}O_9 \cdot HCl \cdot C_2H_6O$, is obtained by treating eupittone with alcoholic hydrochloric acid. The alcohol of crystallisation is only lost after remaining for 11 days in a desiccator, leaving the very hygroscopic hydrochloride.

Eupittone black (hexahydroxyaurin), $O \left\langle \begin{array}{c} C[C_6H_2(OH)_3]_2 \\ C_6H_2(OH)_2 \end{array} \right.$, is prepared by heating eupittone with concentrated sulphuric acid at 110°, when the colour changes from red to blue. It is an amorphous, lustreless powder, soluble in boiling water or alcohol, and with mordants forms a fast black dye. From the alcoholic solution, hydrochloric acid precipitates a *hydrochloride*, $C_{19}H_{14}O_9 \cdot HCl \cdot C_2H_6O$, as a deep blue powder. Partial removal of the methyl groups was not found to be possible.

Hexahydroxy-leucaniline hydriodide, $CH[C_6H_2(OH)_2 \cdot NH_3I]_3 \cdot 2H_2O$, prepared by the action of hydriodic acid and acetic anhydride on eupittone, forms silky, lustrous needles. Concentrated hydrochloric acid converts the hydriodide into a *hydrochloride* crystallising with H_2O .

Oxidation of a solution in acetic acid transforms the leuco-base into hexahydroxyrosaniline, a brilliant blue dye. *Nona-acetylhexahydroxy-leucaniline* forms colourless needles melting at 172—173°.

Formylhexamethoxydimethylleucaniline,



is prepared by the action of methylamine on eupittone, and forms transparent, colourless prisms melting at 187° and soluble in dilute acids. Oxidation of the acid solution converts it into the blue colour-base.

Leuco-eupittone (hexamethoxyleucaurin), $CH \cdot [C_6H_2(OMe)_2 \cdot OH]_3$, obtained by the reduction of the sodium salt of eupittone by zinc dust, crystallises in colourless needles melting and decomposing at 198°. It dissolves in alkalis to a colourless solution, which on boiling becomes blue, with the formation of eupittone. The *triacetate* forms colourless needles melting at 236°.

K. J. P. O.

Eupittone and Pittakal. By CARL LIEBERMANN (*Ber.*, 1901, 34, 1026—1030).—Pittakal, discovered by von Reichenbach (*J. Chem. Physik.*, 1833, 68, 1) is, shown to be a salt of eupittone (hexamethoxyaurin). Reichenbach described it erroneously as a colouring matter capable of mordanting with oxides, with the production of a fast dye, which resembled indigo. The author shows that this is not the case,

as the absence of two hydroxyl groups in the ortho-position to one another would indicate.

K. J. P. O.

2:3-Diaminobenzoic Acid and its Compounds with the Sugars. By BRUNO SCHILLING (*Ber.*, 1901, **34**, 902—907).—The condensation compounds of sugars with 2:3-diaminobenzoic acid have been investigated. The compounds from dextrose and maltose (Griess and Harrow, *Abstr.*, 1888, 267) are probably derivatives of benzimidazole, since, when oxidised with potassium permanganate, they yield the monocarboxylic acid of this substance. The compound from lactose and 2:3-diaminobenzoic acid crystallises in small pyramids and melts at 206°. Owing to the difficulty in purifying these condensation products, they are not suited for the identification of the sugars.

R. H. P.

ψ -Phenylacetic Acid or Norcaradienecarboxylic Acid. By WILHELM BRAREN and EDUARD BUCHNER (*Ber.*, 1901, **34**, 982—997. Compare *Abstr.*, 1900, i, 292, and this vol., i, 85).—Ethyl norcaradienecarboxylate (ethyl ψ -phenylacetate) boiling at 108° under 13 mm. pressure as obtained by fractionation, contains ethyl fumarate and also ethyl β -cycloheptatrienecarboxylate, as the latter is obtained when the ψ -phenylacetate is heated at 150°. On treatment with concentrated sulphuric acid, the ester gives a cherry-red coloration which gradually changes to violet and then to indigo blue. Little or no condensation takes place when methyl diazoacetate is employed in place of the ethyl ester. The pure acid is best obtained by converting the ethyl ester into the amide; the yield of amide is not good even when the ester is left for several weeks in closed vessels with aqueous ammonia saturated at 0°; the chief by-product is β -cycloheptatrienecarbonyl-amide which melts at 157°.

$\Delta^{2,4}$ -Norcaradiene-7-carboxylic acid, $\begin{matrix} \text{CH}:\text{CH}\cdot\text{CH}_2 \\ \text{CH}:\text{CH}\cdot\text{CH}_2 \end{matrix} > \text{CH}\cdot\text{CO}_2\text{H}$, is obtained when the amide is heated with 30 per cent. sulphuric acid and at the same time distilled in steam. It is an oil which solidifies at about -18°, and is stable in the air; the sodium, barium, and magnesium salts are readily soluble, the silver, cupric, and mercurous salts only sparingly. The anilide melts at 141—142°, the dibromide melts and decomposes at 159—160°, is readily oxidised by permanganate, and when treated with zinc dust and acetic acid is reconverted into the original acid. The tetrabromide, 2:3:4:5-tetrabromonorcarane-7-carboxylic acid, $\text{C}_7\text{H}_7\text{Br}_4\cdot\text{CO}_2\text{H}$, melts and decomposes at 233—235°, is not oxidised by permanganate, gives no coloration with concentrated sulphuric acid, and loses its four atoms of bromine when treated with zinc dust and acetic acid.

The chief products formed when norcaradienecarboxylic acid is oxidised with cold acid permanganate are phthalic, benzoic, and trans-1:2:3-trimethylenetricarboxylic acids.

J. J. S.

Mixed Anhydrides. By ÉMILE SEVERIN (*Bull. Soc. Chim.*, 1901, [iii], **25**, 500—510. Compare *Abstr.*, 1900, i, 296 and 598).—According to Béhal (*Abstr.*, 1900, i, 8), when the mixed anhydride of acetic acid and another acid is treated with alcohol, ammonia, phenylhydr-

azine, or hydrochloric acid, the ester, amide, phenylhydrazide, or chloride of acetic acid is formed, whilst the other acid of higher molecular weight is set free. Since a behaviour exactly the reverse of this was observed with the mixed anhydrides studied by the author, a quantity of acetic 3:6-dichloro-2-dimethylaminobenzoylbenzoic anhydride was prepared and carefully purified for detailed examination. The discrepancy between Béhal's and the author's results might readily be explained by the assumption that the author's anhydride was the true anhydride of the acid of higher mol. weight, but the results of analysis, the production of acetic anhydride on distillation under diminished pressure, and other facts, conclusively prove the substance to be a mixed acetic anhydride. The action of ammonia on the anhydride leads to the formation of 3:6-dichloro-2-dimethylaminobenzoylbenzamide, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO} \cdot \text{NH}_2$, which crystallises in thin, white scales melting at 220° . The corresponding *phenylhydrazide*, obtained by the action of phenylhydrazine on the mixed anhydride, crystallises in white scales melting at 196° . The acid *chloride* is produced in small quantity by the action of hydrochloric acid on the mixed anhydride; it crystallises with difficulty. The formation of the methyl and ethyl esters of 3:6-dichloro-2-dimethylaminobenzoylbenzoic acid has already been described (Abstr., 1900, i, 296). From these results, it appears that the introduction of negative groups into the benzene nucleus causes a transference of the activity of the molecule to the radicle of higher molecular weight.

N. L.

Aliphatic- γ and Aromatic-*o*-aldehydo-acids. By AUGUSTIN BISTRZYCKI and C. HERBST (*Ber.*, 1901, **34**, 1010—1021).—The authors point out that most of the reactions described by Anschütz (*Annalen*, 1887, **239**, 177), Hill and Cornelson (Abstr., 1894, i, 319, 320), and Hill and Dunlap (*ibid.*, 1897, i, 571), in favour of the lactone formula for mucobromic acid, can be just as readily explained by the old aldehydo-formula, provided a direct addition of the reagent to the aldehydo-group is assumed, and then subsequent elimination of water. Most of the reactions described in the present paper favour the aldehydo-formula. Mucobromic acid phenylhydrazone (Abstr., 1899, i, 392) crystallises in yellow needles decomposing at $105-106^\circ$. *Mucophenoxybromic acid phenylhydrazone*, $\text{CO}_2\text{H} \cdot \text{C}(\text{OPh}) : \text{CBr} \cdot \text{CH} : \text{N} \cdot \text{NHPh}$, crystallises in deep yellow needles melting and decomposing at 157° , and insoluble in benzene; when boiled with acetic anhydride, it yields 4-bromo-5-phenoxy-1-phenylpyridazone, $\text{OPh} \cdot \text{C} \begin{smallmatrix} \text{CO} \cdot \text{NPh} \\ \text{CBr} \cdot \text{CH} \end{smallmatrix} \text{N}$, which crystallises in yellow needles melting at 115° . *Mucophenoxybromic acid semicarbazone*, $\text{CO}_2\text{H} \cdot \text{C}(\text{OPh}) : \text{CBr} \cdot \text{CH} : \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, melts at 195° , and is only sparingly soluble in the usual solvents. *Mucobromic acid semicarbazone* crystallises in colourless, microscopic prisms melting at 215° ; when crystallised from acetic acid, it yields 4:5-dibromopyridazone melting at 218° , not at 224° as previously stated.

Mucobromic acid benzoylhydrazone, $\text{CO}_2\text{H} \cdot \text{CBr} : \text{CBr} \cdot \text{CH} : \text{N} \cdot \text{NHBz}$, crystallises in felted needles decomposing at $140-141^\circ$. 4:5-Dibromo-1-benzoylpyridazone, $\text{CBr} \begin{smallmatrix} \text{CO} \\ \text{CH} = \text{N} \end{smallmatrix} \text{NBz}$, obtained by the action of

phosphoryl chloride and then water on the benzoylhydrazone, crystallises in colourless prisms decomposing at 187°. *Mucophenoxybromic acid benzoylhydrazone* crystallises from acetone in flat prisms melting and decomposing at 146°, and practically insoluble in the usual solvents. So far, it has not been converted into a pyridazone.

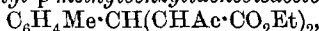
Opianic acid benzoylhydrazone, $C_6H_2(OMe)_2(CO_2H) \cdot CH:N \cdot NHBz$ $[(OMe)_2 : CO_2H : CH = 5 : 6 : 1 : 2]$, forms microscopic crystals melting and decomposing at 227°. *Phthalaldehydic acid benzoylhydrazone*, $CO_2H \cdot C_6H_4 \cdot CH:N \cdot NHBz$, crystallises in colourless prisms or plates melting and decomposing at 189°.

Opianic acid N-phenyloxime, $C_6H_2(OMe)_2(CO_2H) \cdot CH < \begin{smallmatrix} NPh \\ O \end{smallmatrix}$, obtained by boiling a solution of opianic acid and phenylhydroxylamine in absolute alcohol, crystallises in flat needles melting at 174°, and insoluble in benzene or light petroleum, but readily soluble in sodium carbonate solution. Opianic acid and *p*-aminophenol react, forming *opianylidene-p-hydroxyaniline*, $CO_2H \cdot C_6H_2(OMe)_2 \cdot CH:N \cdot C_6H_4 \cdot OH$, which crystallises in glistening plates melting at 223°, and only sparingly soluble in the usual solvents; as it is readily soluble in sodium carbonate solution, it cannot have a lactonic constitution (compare Liebermann, Abstr., 1896, i, 132). *Bromo-opianic acid N-phenyloxime*, forms glistening prisms. *Phthalaldehydic acid N-phenyloxime* forms colourless needles decomposing at 125° after drying at 80°. Both mucobromic and mucophenoxybromic acid react with phenylhydroxylamine, but the products are oily.

Mucobromic acid ethylenediamine, $C_6H_5O_2N_2Br_2$, decomposes at 117°, and is insoluble in organic solvents, but dissolves in sodium carbonate solution. Mucobromoamide, when treated with concentrated sulphuric acid, yields an *anhydride*, $\begin{smallmatrix} CBr \cdot CO \\ | \\ CBr \cdot CH \end{smallmatrix} > N$, melting at 153°. J. J. S.

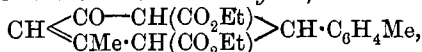
isoAlantolactone, a Constituent of the Root of *Inula Helenium*. By JULIUS SPRINZ (*Arch. Pharm.*, 1901, 239, 201—213).—This paper is almost identical with one already published (this vol., i, 325). *isoAlantolic acid* melts at the same temperature as its lactone, and its calcium salt crystallises from a hot dilute solution with $2\frac{1}{2}H_2O$. C. F. B.

Ethyl p-Methylbenzylideneacetoacetate. By BERNHARD FLÜRSCHHEIM (*Ber.*, 1901, 34, 787—791. Compare Knoevenagel, Abstr., 1895, i, 48, &c.).—When *p*-tolualdehyde is mixed with ethyl acetoacetate and a little diethylamine, the mixture heated to 40° and allowed to remain for several weeks, *ethyl-p-methylbenzylidenebisacetoacetate*,

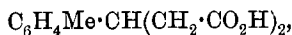
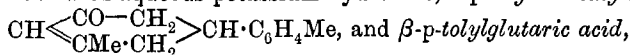


melting at 132.5° is formed. In one experiment, when but a little diethylamine was added at first, *ethyl p-methylbenzylideneacetoacetate*, $C_6H_4Me \cdot CH : CAc \cdot CO_2Et$, melting at 74°, was obtained quite unexpectedly. By heating this substance with ethyl β -aminocrotonate and a little alcohol at 100°, *ethyl 4-p-tolyl-2 : 6-dimethyldihydropyridine-3 : 5-dicarboxylate*, $NH < \begin{smallmatrix} CMe : C(CO_2Et) \\ CMe : C(CO_2Et) \end{smallmatrix} > CH \cdot C_6H_4Me$, melting at 138°, is

obtained. When the bisacetoacetate is dissolved in absolute alcohol and the solution saturated with gaseous hydrogen chloride, *ethyl 5-p-tolyl-3-methylcyclohexenone 4:6-dicarboxylate*,



melting at 84—85° is formed. When the bisacetoacetate is heated at 100° with aqueous potassium hydroxide, *5-p-tolyl-3-methylcyclohexenone*,



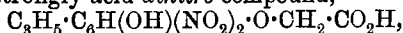
are formed; the latter melts at 164—165°; the former melts at 42—43°, and boils at 198—202° under a pressure of 16 mm., whilst its *oxime* melts at 125—126°. When the potash solution is concentrated, more of the glutaric acid is obtained; when it is dilute, more of the hexenone; a liquid product boiling and decomposing at 70—80° is also obtained, possibly an unsaturated fatty acid. C. F. B.

Eugenolglycollic Acid [Eugenoxylacetic Acid]. By ROBERT CLAUSER (*Monatsh.*, 1901, 22, 123—144).—It is shown that the eugenoxylacetic acid (m. p. 81°) obtained by previous investigators contained water of crystallisation ($1\text{H}_2\text{O}$). On drying in a vacuum or recrystallising from anhydrous solvents, the anhydrous acid melting at 100° is obtained. The *potassium* salt, $\text{C}_{12}\text{H}_{13}\text{O}_4\text{K} \cdot \frac{1}{2}\text{H}_2\text{O}$, forms long needles; the *barium* salt crystallises in needles with $2\text{H}_2\text{O}$; the *zinc* and *copper* salts are crystalline precipitates, containing respectively 4 and $2\text{H}_2\text{O}$, whilst the *silver* salt is an anhydrous crystalline powder. The *methyl* ester forms colourless crystals melting at 43° and boiling at 161—164° under 19 mm. pressure. The *ethyl* ester forms large, white crystals melting at 36—37° and distilling at 200—205° under 19 mm. pressure. The *amide*, crystallises from water in needles melting at 110°. The *anilide* crystallises from petroleum in rectangular rhombic plates melting at 58°. The *phenylhydrazide*, forms slightly yellow plates melting at 113°.

On brominating eugenoxylacetic acid in chloroform solution, two substances are obtained. They are separated by crystallising from aqueous potassium carbonate, in which, when cold, only *dibromo-eugenoxylacetic acid* is soluble, whilst the other compound, $\text{C}_{12}\text{H}_{13}\text{Br}_2\text{O}_5$ (?), which forms needles melting at 153—154°, crystallises out. The acid crystallises in needles melting at 93—94°; *methyl dibromo-eugenoxylacetate* forms needles melting at 70°; the *amide*, obtained from the methyl ester or by brominating eugenoxylacetamide, crystallises in needles melting at 85°.

Diiodo-eugenoxylacetic acid is obtained by the action of iodine on a chloroform solution of the acid in the form of very unstable crystals which decompose at 96°.

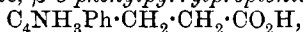
Nitro-eugenoxylacetic acid is prepared by the carefully regulated action of nitric acid on eugenoxylacetic acid in acetic acid solution; it crystallises in rosettes of needles melting at 115—116°. With excess of nitric acid a strongly acid *dinitro*-compound,



is obtained as very insoluble yellow needles melting and decomposing at 154°.

K. J. P. O.

Phenacyllævulic Acid and a new Carboxylic Acid, $C_{13}H_{13}O_3N$, of the Pyrrole Group. By EDUARD A. KEHRER (*Ber.*, 1901, 34, 1263—1268. Compare Abstr., 1899, i, 568).—The *potassium, sodium, calcium, silver*, and *zinc* salts of phenacyllævulic acid are described. The *dioxime*, $C_{13}H_{16}O_4N_2$, melts at 144° . By heating with acetic acid and ammonium acetate, *β -5-phenylpyrrylpropionic acid*,



is produced, which crystallises from chloroform or ether in hexagonal plates and melts at 140 — 141° ; the silver and calcium salts are also described.

T. M. L.

Le Royer's Dichlorophthalic Acid. By ÉMILE SEVERIN (*Bull. Soc. Chim.*, 1901, [iii], 25, 499—500).—The dichlorophthalic acid previously studied by the author (Abstr., 1900, i, 296) and assumed, on Le Royer's authority, to be an *ortho*-derivative, has since been shown by Graebe (Abstr., 1900, i, 546) to be in reality the *para*-acid.

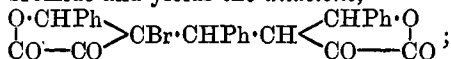
N. L.

***p*-Hydroxyhydratropic Acid.** By J. BOUGAULT (*Compt. rend.*, 1901, 132, 976—978. Compare Abstr., 1900, i, 495, 548).—*p*-Hydroxyhydratropic acid, first obtained by Trinius (compare Abstr., 1885, 529), is readily prepared by digesting on the water-bath a mixture of *p*-methoxyhydratropic acid, iodine, red phosphorus, and concentrated hydriodic acid. It crystallises in colourless prisms melting at 130° , and readily dissolves in the ordinary organic solvents, 2.5 parts being soluble in 100 parts of water at 12° . The substance, when obtained by the preceding process, is a racemic compound, and may be split into its optical constituents by means of morphine, the salt of the levorotatory acid with this alkaloid being less soluble in water than that of the dextrorotatory compound. *l-p*-Hydroxyhydratropic acid has $[\alpha]_D - 71^\circ$. Saturated aqueous solutions of the acid yield precipitates with lead and mercurous acetates, but not with silver nitrate; ferric chloride develops a bluish-green coloration, which becomes brown on adding sodium hydroxide. The juice of *Russula delica* oxidises the acid developing a red coloration. The sodium, potassium, barium, calcium, and magnesium salts are very soluble; the zinc salt dissolves in less than 10 parts of cold water, whereas zinc *p*-hydrocoumarate requires for its solution 130 parts of this solvent. The *dibromide*, *diiodide*, and the *methyl* and *ethyl* esters of *p*-hydroxyhydratropic acid melt at 115° , 149° , 57° , and 68° respectively; they are prepared by methods identical with those employed in the case of the corresponding derivatives of *p*-hydrocoumaric (phloretic) acid, and the paper includes a table comparing the melting points of the two series. G. T. M.

Occurrence of Quinic Acid. By EDMUND O. VON LIPPMANN (*Ber.*, 1901, 34, 1159—1162).—A small amount of Hesse's quinide (*Annalen*, 1859, 110, 335) has been isolated from the alcoholic extract of a powder deposited when beetroot leaves are dried at a moderate temperature. When hydrolysed with alkalis, it yields *i*-quinic acid; when an aqueous solution of this is left exposed to the atmosphere, fermentation begins, and *d*-quinic acid is left. It melts at 164° , and has $[\alpha]_D + 44^\circ$ at 20° .

A substance, *betitol*, $C_6H_{12}O_4$, has been isolated from beetroot extract after removal of the sugar; it crystallises in colourless prisms, melts at 224° , is readily soluble in water, has a dextro-rotatory power, and on oxidation yields quinone. J. J. S.

Condensation of Pyruvic Acid with Benzaldehyde. By EMIL ERLÉNMEYER, jun. (*Ber.*, 1901, **34**, 817—821. Compare Abstr., 1899, i, 601).—The gelatinous substance formed along with cinnamylformic acid by the action of benzaldehyde on pyruvic acid (Claisen and Claparède, Abstr., 1882, 520) is apparently the sodium salt of an *acid*, $O\cdot CHPh \begin{smallmatrix} \diagup \\ CO-CO \end{smallmatrix} > CH\cdot CHPh\cdot C(CHPh)\cdot CO\cdot CO_2H$, which, when liberated by hydrochloric acid, separates from alcohol in efflorescent crystals of the composition $3C_{27}H_{20}O_6, 4C_6H_6O$, and on adding light petroleum is precipitated from its chloroform solution in lustrous needles melting at 208° ; the *sodium* salt, $C_{27}H_{19}O_6Na, C_6H_6O$, crystallises from alcohol in long, colourless needles. The acid combines readily with bromine in chloroform solution to form, probably, the *dibromide*, $O\cdot CHPh \begin{smallmatrix} \diagup \\ CO-CO \end{smallmatrix} > CH\cdot CHPh\cdot CBr(CHBrPh)\cdot CO\cdot CO_2H$, initially, but this loses hydrogen bromide and yields the *dilactone*,



the latter crystallises from alcohol in long, colourless needles which decompose at $196-197^\circ$. W. A. D.

Acetals of *p*-Diketohexamethylene. By ROBERT STOLLÉ (*Ber.*, 1901, **34**, 1344—1345).—By heating ethyl succinylsuccinate with ethyl alcohol at 200° , there is obtained together with greenish-yellow crystals melting at $132-133^\circ$, the *acetal* of 1:4-diketohexamethylene, $C_{14}H_{28}O_4$, which forms colourless plates melting at 89° . Alcohol is eliminated on heating. The *methylacetal* melts at $80-81^\circ$. The ethyl derivative is also formed when *p*-diketohexamethylene is heated with ethyl alcohol. K. J. P. O.

Chemical Action of Light. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Atti. Real. Accad. Lincei*, 1901, [v], **10**, i, 228—233. Compare this vol., i, 36).—When *o*-nitrobenzaldehyde is exposed, either in benzene, ether, or acetone solution, or spread out in a thin layer on the walls of a flask to the action of sunlight, it is converted into *o*-nitrosobenzoic acid. In ethyl alcohol solution, *ethyl o*-nitrosobenzoate is obtained in well-developed, colourless crystals melting at $120-121^\circ$; when dissolved or melted, the salt gives rise to a green liquid. As *o*-nitrosobenzoic acid does not undergo esterification when exposed in alcoholic solution to the action of light, the reaction between the *o*-nitrobenzaldehyde and alcohol probably results first in the formation of the compound $NO_2\cdot C_6H_4\cdot CH(OH)\cdot OEt$, which is then converted by way of the nitroso-derivative, $NO\cdot C_6H_4\cdot C(OH)_2\cdot OEt$, into ethyl *o*-nitrosobenzoate and water. *Methyl o*-nitrosobenzoate, prepared by the action of sunlight on a methyl alcoholic solution of *o*-nitrobenzaldehyde, crystallises from methyl alcohol in large, rhombic plates, which melt at

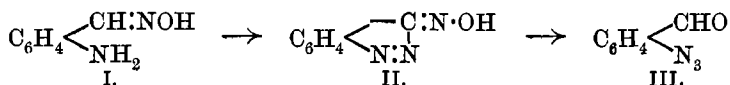
152—153° giving an emerald green liquid. An *isopropyl* alcoholic solution of *o*-nitrobenzaldehyde yields *o*-nitrosobenzoic acid and not the *isopropyl* ester.

The action of sunlight on a paraldehyde solution of *o*-nitrobenzaldehyde yields, besides *o*-nitrosobenzoic acid, small quantities of a *compound* having the composition $C_9H_7O_3N$, which crystallises from alcohol in large, colourless prisms melting at 121° and is being further investigated.

When exposed to sunlight in alcoholic solution, neither *m*- nor *p*-nitrobenzaldehyde yields definite products.

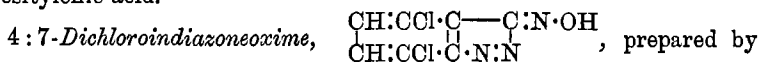
T. H. P.

***o* Aminobenzaldoximes.** By EUGEN BAMBERGER and E. DEMUTH (*Ber.*, 1901, **34**, 1309—1339. Compare *Abstr.*, 1899, i, 123).—On diazotising *o*-aminobenzaldoxime (I), condensation of the neighbouring diazo- and aldoxime groups takes place: a condensation which is in no way analogous to the Beckmann transformation of oximes. By the action of alkali hydroxides or hot water, the indiazoneoxime (II), thus produced, is converted into *o*-triazobenzaldehyde (III) (called by the authors, "*o*-azidobenzaldehyde"). The latter on oxidation yields the corresponding acid, which has been synthesised from anthranilic acid.



The *o*-triazobenzaldehydes are colourless, well crystallised substances, very readily volatile in steam and possessing a powerful and characteristic smell.

2-Triazo-3:5-dimethylbenzaldehyde, $N_3 \cdot C_6H_2Me_2 \cdot CHO$, prepared by the carefully regulated action of *N* solution of sodium hydroxide on 5:7-dimethylindiazoneoxime (*loc. cit.*), crystallises from petroleum in long, silky, lustrous needles melting at 33·5—34°. It dissolves directly in aqueous sodium hydrogen sulphite and is again precipitated by sodium carbonate. The *p*-nitrophenylhydrazones, crystallises in lustrous orange needles, melting at 153·5—156·5°. Oxidation by means of a 1 per cent. solution of potassium permanganate produces 2-triazo-3:5-dimethylbenzoic acid, $N_3 \cdot C_6H_2Me_2 \cdot CO_2H$, which crystallises in needles melting and decomposing at 156°. This acid was also synthesised from 2-aminomesitylenic acid by treating the diazonium perbromide obtained from the latter with concentrated aqueous ammonia. By boiling the triazodimethylbenzaldehyde for 8 hours with excess of *N* sodium hydroxide, it is mainly converted into 2-aminomesitylenic acid.



the action of sodium nitrite on 2-amino-3:6-dichlorobenzaldoxime dissolved in acetic acid, crystallises from xylene in needles of a golden-bronze colour, melting and decomposing at 168·5° (*corr.*). Warm dilute mineral acids decompose this compound, whilst alkali hydroxides slowly dissolve it, forming a yellow solution which rapidly becomes colourless. This change of colour is accompanied by the separation of an oil, which is

2-triazo-3:6-dichlorobenzaldehyde, $C_6H_2Cl_2 \cdot N_3 \cdot CHO$. From petroleum, this substance crystallises in needles melting at $86-86.3^\circ$ (corr.). The *p-nitrophenylhydrazone* forms orange-yellow needles, which decompose at 155° , and when heated at 170° , nitrogen is evolved, and a compound, $C_{13}H_8O_2N_4Cl_2$, which is probably a phenotriazine, is obtained. It crystallises in golden-yellow needles melting at $233-234^\circ$ (corr.). *3:6-Dichloroanthranilic acid*, obtained by the action of alkalis on the triazaldehyde, forms white needles melting at $154.5-155^\circ$ (corr.).

Dibromo-o-aminobenzaldoxime, $NH_2 \cdot C_6H_2Br_2 \cdot CH \cdot NOH$, prepared from the aldehyde (see below), crystallises in needles melting at 189° (corr.). *Dibromoindiazoneoxime* forms golden-yellow needles, which begin to decompose at 178° and explode at 182° (corr.). *Dibromo-o-triazobenzaldehyde*, $N_3 \cdot C_6H_2Br_2 \cdot CHO$, forms white, silky needles melting at $75.5-76^\circ$ (corr.). From it can be obtained *dibromoanthranilic acid*, $NH_2 \cdot C_6H_2Br_2 \cdot CO_2H$, which crystallises in needles melting and decomposing at $235-236^\circ$ (corr.).

Indiazoneoxime (II) is prepared from *o-aminobenzaldoxime* by diazotising in the presence of concentrated hydrochloric acid; it forms golden-yellow needles melting and decomposing at $160-160.5^\circ$ (corr.). When *o-aminobenzaldoxime* is diazotised in the presence of dilute hydrochloric acid, *o-aldoximophenylazo-o-aldoxihoanilide*, $C_{14}H_{13}O_2N_5$, is obtained as a yellow, amorphous solid which decomposes at $73-74^\circ$. *o-Triazobenzaldehyde*, $N_3 \cdot C_6H_4 \cdot CHO$, prepared from *indiazoneoxime*, crystallises in transparent, thick plates melting at 37.5° . The *phenylhydrazone* forms pale yellow prisms melting at $101.5-102^\circ$; the *p-nitrophenylhydrazone* forms orange red needles melting and decomposing at $191-192^\circ$. *o-Triazobenzaldoxime* crystallises in colourless needles melting at $103-103.5^\circ$, is soluble in alkalis, and hydrolysed by dilute sulphuric acid. On oxidation, *o-triazobenzaldehyde* yields *o-triazobenzoic acid*, identical with the acid synthesised from anthranilic acid by Griess. Anthranilic acid can be obtained from the triazobenzaldehyde by the prolonged action of boiling aqueous sodium hydroxide.

The paper contains a detailed description of the preparation of *o-aminobenzaldehyde*, the *p-nitrophenylhydrazone* of which forms lustrous red leaflets melting at 218° .

Dibromo-o-aminobenzaldehyde, prepared by treating with concentrated ammonia the diazonium perbromide, $C_6H_4N_2Br_3 \cdot CHO$, obtained from *o-aminobenzaldehyde*, crystallises in elongated light, yellow prisms melting at $137-137.5^\circ$. No triazobenzaldehyde is formed in this reaction.

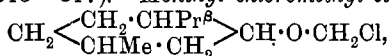
K. J. P. O.

Preparation of Aldehydes $R \cdot CHMe \cdot CHO$ by Means of Cyclic Hydrocarbons containing Propenylic Side Chains, such as Anethole, isoSafrole, &c. By J. BOUGAULT (*Bull. Soc. Chim.*, 1901, [iii], 25, 446-448. Compare Abstr., 1900, i, 495, 641).—In the preparation of aldehydes by oxidising anethole, isosafrole, &c., with a mixture of iodine and mercuric oxide, as previously described (Abstr., 1900, i, 495), a considerable portion of the aldehyde combines with the alcohol employed. This inconvenience may be avoided by working in moist ethereal, instead of alcoholic, solution.

N. L.

Action of Mixed Organomagnesium Compounds on Naphthyl Methyl Ketones. By VICTOR GRIGNARD (*Bull. Soc. Chim.*, 1901, [iii], 25, 497—499. Compare this vol., i, 250 and 263).—Magnesium methyl iodide reacts with α -naphthyl methyl ketone in ethereal solution to form α -naphthyl dimethyl carbinol, which crystallises in slender needles melting at 80° . When warmed with acetic anhydride, it yields $\beta\alpha$ -naphthyl propylene, $\text{CH}_2\text{:CMe}\cdot\text{C}_{10}\text{H}_7$, a colourless liquid boiling at 125° under 8 mm. pressure which has a sp. gr. 1.0208 at 0° , $n_D = 1.61435$ at 9° , and forms a *picrate* crystallising in yellow needles melting at 91° . The action of magnesium methyl iodide on β -naphthyl methyl ketone results in the formation, not of the corresponding carbinol, but of $\beta\beta$ -naphthyl propylene, which crystallises in white, nacreous scales melting at 46 — 47° , boils at 138 — 140° under 7 mm. pressure, and forms a *picrate* crystallising in orange-yellow needles melting at 88° . β -Naphthyl isoeptylene, obtained by the action of isoamyl magnesium bromide, is a colourless liquid which boils at 175 — 178° under 10 mm. pressure, has a sp. gr. 0.9808 at 0° and $n_D = 1.59124$ at 9° , and forms a *picrate* crystallising in microscopic, orange needles melting and decomposing at 46 — 47° . It appears from these results that tertiary β -naphthyl carbinols are unstable and undergo dehydration at the moment of their formation. N. L.

Action of Formaldehyde on Menthol. By EDGAR WEDEKIND (*Ber.*, 1901, 34, 813—817).—*Menthyl chloromethyl ether*,



prepared by saturating a cooled mixture of menthol and 40 per cent. aqueous formaldehyde with gaseous hydrogen chloride, boils at 160 — 162° under 16 mm. pressure and at 230° with partial decomposition under the ordinary pressure, has a sp. gr. 0.9821, and in chloroform has $[\alpha]_D - 172.57^\circ$ at 21° ; the refractive index is given for the principal lines of the spectrum, n_D being 1.465 at 19° . It is very sensitive to moisture, being rapidly resolved into its components, menthol, formaldehyde, and hydrogen chloride, after the manner of the chlorinated aliphatic ethers, the action in the latter case, however, being far more rapid. On warming with sodium β -naphthoxide in xylene solution, *menthyl β -naphthyl methylene ether*, $\text{C}_{10}\text{H}_{19} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_{10}\text{H}_7$, melting at 120° , is obtained as a non-crystallisable powder.

Dimethylmenthylal, $\text{CH}_2(\text{O} \cdot \text{C}_{10}\text{H}_{19})_2$, prepared by distilling menthyl chloromethyl ether with menthol, crystallises from dilute alcohol in felted needles, melts at 57° (Brochet's "*dimentholformal*," *Abstr.*, 1899, i, 530, melts at 56.5°), has $[\alpha]_D - 77.94^\circ$ at 24° , and is indifferent to boiling acids and alkalis; it has no physiological action, passing through the body unchanged. W. A. D.

Biological Oxidation of Fenchone. By ENRICO RIMINI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 244—249).—The urine of a dog to which camphor has been administered for some time has been found to contain α - and β -camphoglycuronic acids, and a third acid, to which the name uraminocamphoglycuronic acid has been given; the camphoglycuronic acids can be resolved into glycuronic acid and a compound

called camphorol, of the constitution $C_{18}H_{14} \begin{matrix} < CH \cdot OH \\ CO \end{matrix}$. The author has carried out similar experiments with fenchone, which was administered to a dog whose urine was examined to see if products analogous to those obtained in the case of camphor could be found in it. No fenchoneglycuronic acid could be isolated owing to the small quantity of material available, but the presence of such an acid is shown by boiling the liquid with dilute sulphuric acid, by which means a dense, oily liquid was obtained; this gradually deposited acicular crystals of a compound which on purification melts at 89° and has the composition $C_{10}H_{16}O_2$. This substance, which is an isomeride of camphorol, is saturated, but is not of an alcoholic or an acid nature. It must be regarded as an oxyfenchone, and is probably analogous with the isomeric compound obtained by Czerny (Abstr., 1900, i, 675) by dissolving fencholenic acid in concentrated sulphuric acid and pouring the liquid on to ice.

T. H. P.

Surface Tension and Viscosity of some Essential Oils. By PAUL JEANCARD and SATIE (*Bull. Soc. Chim.*, 1901, [iii], 25, 519—523).—The surface tension and viscosity of a number of essential oils were determined by Duclaux's method, and the results obtained are given in tabular form. The following general conclusions are arrived at for the different classes of oils. *Alcohol group*.—Oils consisting chiefly of geraniol, free or combined, have a higher surface tension than those having linalool for their principal constituent. The viscosity of esters is much less than that of the corresponding alcohols. Diminution of viscosity generally corresponds with an increase in the saponification number. *Phenol group*.—With oils containing eugenol, the surface tension decreases with the proportion of phenols. The non-phenolic portions of oils containing thymol and carvacrol have a lower viscosity and surface tension than the phenolic portions. *Aldehyde group*.—The surface tension diminishes with the percentage of aldehydes. The viscosity of the aldehydes is generally lower than that of the corresponding alcohols. A few figures are also given for some oils of the ketone and hydrocarbon groups.

N. L.

Ethereal Oils. By SCHIMMEL and Co. (*Chem. Centr.*, 1901, i, 1006—1008; from *Geschäftsber.*, April, 1901).—Alpinia oil, prepared by distilling the fresh leaves of *Alpinia malaccensis*, has a sp. gr. 1.02 at 26° , a rotatory power $+6.5^{\circ}$, contains methyl cinnamate and about 25 per cent. of compounds which cannot be hydrolysed (compare van Romburgh, this vol., i, 219). From the latter, *d*-pinene was isolated. *d*-Pinene nitrosochloride melts at 108° , and not at 103° as usually stated.

The aqueous distillate of oil of bay contains methyl alcohol, furfuraldehyde, and diacetyl.

The fractions of higher boiling point and the residue obtained by distilling a French bitter fennel oil contained a substance which separates from alcohol or ethyl acetate in small crystals and melts at 164 — 165° .

A ketone has been isolated from oil of cassia flowers (*Acacia*

Farnesiana) which is probably related to ionone; it has the odour of violets and boils at about 133°. It combines with semicarbazide, forming a compound which crystallises in white prisms and melts at 200°, and with *p*-bromophenylhydrazine a compound which melts at 103—107°. The lower fractions of the oil apparently contain benzyl alcohol.

Dowdard's viscosity test (Abstr., 1900, i, 676) is not applicable to oil of lemon as the viscosities of citrene and of oil of lemon are too nearly alike, and tests with different Reischauer viscometers give different results.

Eucalyptus oil from *Eucalyptus aggregata* has a sp. gr. 0.956 and saponification number 112. According to Smith (*J. Proc. Roy. Soc. New South Wales*, 1900, 34, 72), it contains *d*-pinene and amyl eudesmate, $C_{13}H_{17} \cdot CO_2 \cdot C_5H_{11}$. Eudesmic acid, $C_{13}H_{17} \cdot CO_2H$, is an unsaturated acid, crystallises from alcohol in rhombic prisms, and combines with bromine to form a compound which melts at 102—103°. The oil contains neither phellandrene nor cineol. Eucalyptus oil from *Eucalyptus patentinervis* contains citral and probably linalool and geraniol and their esters (compare this vol., i, 282).

Linaloes oil prepared from guayana or cayenne-linaloe wood, has a sp. gr. 0.872—0.875 at 14.5°, $[\alpha]_D -15$ — -16° at 13°, and dissolves in 2 parts of 70 per cent. alcohol. It consists almost entirely of *l*-linalool (Theulier, *Rev. gén. Chim. pur. appl.*, 1900, 3, 262). The physical constants of two German and four Bulgarian rose oils are given in a table in the original paper; the German oils have a lower specific gravity and a smaller rotatory power, but contain more stearoptene. The terpeneol which is used in elder perfume, not only contains the inactive terpeneol which melts at 35—36°, but also another inactive terpeneol, $OH \cdot CMe < \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} > CH \cdot CMe \cdot CH_2$, of a different odour.

The latter forms needles, boils at 90° under 10 and at 209—210° under 752 mm. pressure, has a sp. gr. 0.923 at 15° and $n_D 1.4747$ at 20°. The *phenylurethane*, $C_{17}H_{23}O_2N$, melts at 85°. The *nitrosochloride* melts at 102—103° and does not readily react with amines. When this terpeneol is oxidised first by permanganate and then by chromic acid, it does not yield a ketolactone but an *oxyketone*, $C_9H_{16}O_2$, which boils at 140—145° under 19 mm. pressure and has a sp. gr. 1.023 at 20° and $n_D 1.47548$ at 20°. The *semicarbazone*, $C_{10}H_{19}O_2N_3$, melts at 195—196°. By the action of bromine and sodium hydroxide solution on the ketone, a *hydroxy-acid*, $C_8H_{14}O_3$, is formed; it melts about 130°, and on warming with concentrated sulphuric acid yields *p*-toluic acid. Wartara oil contains methyl cinnamate.

The paper also contains references to bergamot, atlas cedar, and calamint oils which are not of chemical interest. E. W. W.

Crystalline Component of Calamus Oil. By HUGO VON SODEN and WILHELM ROJAHN (*Chem. Centr.*, 1901, i, 893—894; from *Pharm. Zeit.*, 46, 243).—A compound, $C_{15}H_{26}O_2$, has been isolated from a Galician calamus oil. It crystallises from methyl alcohol, melts at 165—166°, sublimes at 105—110° without loss of water, is only slightly soluble in the ordinary solvents, and has neither acid nor basic pro-

erties. With hydrogen chloride and bromine, it forms additive compounds, and it is not attacked by boiling with acetic anhydride.

E. W. W.

Constituents of Calamus Oil. By HERMANN THOMS and R. BECKSTROEM (*Ber.*, 1901, **34**, 1021—1023).—A fraction of calamus oil, which distilled between 272° and 340° under atmospheric pressure, and had a sp. gr. 1.0254 at 20°, was hydrolysed with alcoholic potash, and the product fractionated under reduced pressure. The portion of highest boiling point, when kept, deposited crystals of a compound, $C_{15}H_{26}O_2$, which melted at 166—167.5°. From the alcoholic mother liquor from which this compound separated, asarone was obtained. On extracting the calamus oil with a solution of sodium hydrogen sulphite, an oil is obtained from which crystals of asarylaldehyde slowly separate.

K. J. P. O.

Essence of Geranium from Cannes. By PAUL JEANCARD and SATIE (*Bull. Soc. Chim.*, 1901, [iii], **25**, 516—519. Compare Abstr., 1900, i, 242).—On an average, six specimens per week of essence of geranium from Cannes were examined during the season of 1900, and the minimum, maximum, and mean weekly values of the sp. gr., rotatory power, solubility in 70 per cent. alcohol, surface tension, viscosity, saponification number (hot and cold), free and total alcohols, and ethereal salts are given in the paper in tabular form. The mean results differ but little from those previously obtained (*loc. cit.*). Analyses were also made of the oil after treatment in various ways. Neutralisation diminishes the sp. gr., rotatory power, and surface tension, but increases the solubility. Acetylation increases the sp. gr. and surface tension, but diminishes the viscosity and solubility. Saponification increases the viscosity and solubility. There appears, therefore, to be a connection between the greater solubility and less acidity of the essence from Cannes, as compared with other varieties. The greater part of the free acid is derived from the leaves. N. L.

Essential Oil of Female Rose Wood. By EUGÈNE THEULIER (*Bull. Soc. Chim.*, 1901, [iii], **25**, 468—475).—The wood *Licaria guanensis*, or female rose wood, when distilled with steam yields about 1.5 per cent. of a colourless oil of characteristic odour, having a sp. gr. 0.8727—0.875 at 14.5°, rotatory power -15.2° to -15.5° at 13°, and saponification number 1.385; it is soluble in two volumes of 70 per cent. alcohol, and distils between 192° and 210°. The oil consists almost entirely of *l*-linalool, with less than 1 per cent. of esters which could not be identified; methylheptenone is absent. N. L.

Algerian Oil of Rue. By HUGO VON SODEN and KARL HENLE (*Chem. Centr.*, 1901, i, 1006; from *Pharm. Zeit.*, **46**, 277).—An Algerian oil of rue has been found to possess properties differing from those of the ordinary oil. Its odour not only resembled that of rue, but was also somewhat similar to that of fatty ketones. It had a sp. gr. 0.842 at 15°, a rotatory power -5° (100 mm. tube), a saponification number 64, and consisted mainly of *methyl heptyl ketone*, together with a small quantity of methyl nonyl ketone, and esters of unknown

alcohols. The methyl heptyl ketone, $\text{COMe}\cdot\text{C}_7\text{H}_{15}$, is probably the normal ketone; it is a colourless oil, boils at $193\text{--}194^\circ$ under 740 mm. pressure, has a sp. gr. 0.821 at 20° , and solidifies at -15° . The *semi-carbazone*, $\text{C}_7\text{H}_{15}\cdot\text{CMe}\cdot\text{CH}_3\text{ON}_3$, crystallises in lustrous leaflets and melts at $118\text{--}119^\circ$.
E. W. W.

Essential Oil of Vetiver. By EUGÈNE THEULIER (*Bull. Soc. Chim.*, 1901, [iii], 25, 454—465).—Essential oil of vetiver, *iwaran-cusa*, or *cuscus*, obtained by steam distillation from the roots of *Andropogon Muricatus*, is a dark, greenish-brown, viscous liquid, soluble in 1.5 vols. of 80 per cent. alcohol. Two specimens distilled (1) at Grasse, and (2) at Reunion gave the following results:

| | (1) | (2) |
|------------------------------------|-----------------|--------------|
| Sp. gr. at 20° | 1.0091 | 0.986 |
| Rotatory power at 20° | + 35.10° | + 28° |
| Acid number | 32.48 | 6.16 |
| Saponification number | 11.92 | 12.12 |

The acidity of the oil appears to be due to an acid corresponding with a sesquiterpenic alcohol. From the behaviour of the oils on fractional distillation, it is concluded that the two varieties contain the same constituents, but in different proportions.
N. L.

The Resin of Pinus Sylvestris. By ALEXANDER TSCHIRCH and B. NIEDERSTADT (*Arch. Pharm.*, 1901, 239, 167—181).—The sample examined was collected in Finland it had acid number about 161, saponification number equal to this, and iodine number 65.7. By distilling it, traces of succinic acid were obtained, and a *bitter substance* was extracted with hot water.

From an ethereal solution of the resin, ammonium carbonate solution extracts nothing. A mixture of acids is extracted by 1 per cent. aqueous sodium carbonate. From a solution of these in a mixture of methyl and ethyl alcohols, *silveolic acid*, $\text{C}_{14}\text{H}_{20}\text{O}_2$, crystallises; this melts at 138° , and has acid (and saponification) number 262 (corresponding with monobasicity), and iodine number 57.7 (corresponding with the formation of a monoiodo-compound); its crystalline *potassium* and *barium* salts were analysed. The other acids are amorphous, but form lead salts that are respectively insoluble and soluble in alcohol, and thus can be separated. The former, *α -silvinolic acid*, $\text{C}_{15}\text{H}_{26}\text{O}_2$, melts at $85\text{--}90^\circ$, has acid (and saponification) number 232 (corresponding with monobasicity), and iodine number 53.3 (corresponding with the formation of a monoiodo-compound). The second acid *β -silvinolic acid*, $\text{C}_{14}\text{H}_{24}\text{O}_2$, melts at $89\text{--}95^\circ$, and has acid (and saponification) number 247 (corresponding with monobasicity), and iodine number 56.5 (corresponding with the formation of a monoiodo-compound). From the residual ethereal solution after the removal of these acids, aqueous potassium hydroxide extracts nothing further.

The ether was distilled off and the residue distilled with steam, when an *essential oil* passed over, boiling at $155\text{--}163^\circ$, and with a sp. gr. 0.840.

There remained indifferent *silvoren*, melting at $58\text{--}60^\circ$.

In 100 parts of the drug there are contained:—silveolic acid, 1.5;

silvinolic acids, α and β , 58—60; essential oil 15; silvoren 20—21; bitter substance, succinic acid, and impurities 1—2. C. F. B.

New Zealand Kauri Copal from Dammara Australis. By ALEXANDER TSCHIRCH and B. NIEDERSTADT (*Arch. Pharm.*, 1901, **239**, 145—167).—The sample examined was a recent fossil specimen of Kauri copal from New Zealand; it melted at 110—125°, had acid number about 107, saponification number only slightly higher, and iodine number 45·7. When it is distilled, only 2 per cent. of carbon remains in the retort; acetic and formic acids can be detected in the distillate, but not succinic acid. A bitter substance can be extracted with water.

From an ethereal solution of the copal, 1 per cent. aqueous ammonium carbonate extracts *kauric acid*, $C_{10}H_{16}O_2$. This melts at 192°, has a specific rotation 51·7° in 2 per cent. alcoholic solution, acid (and saponification) number 332·5 (corresponding with monobasicity) and iodine number 75·8 (corresponding with the formation of a monoiodo-compound); the anhydrous potassium and lead salts were analysed. Oudemans' podocarpic acid, $C_{17}H_{22}O_3$ (*Onderz. Naturk. Verh. K. Akad. Wetensch. Amsterdam*, 1873, **14**), resembles kauric acid in some respects, but has acid (and saponification) number 205, and iodine number 46·1.

From the ethereal solution, 1 per cent. aqueous sodium carbonate now extracts amorphous isomeric α - and β -*kaurolic acids*, $C_{12}H_{20}O_2$, the lead salts of which are respectively insoluble and soluble in alcohol. The acids melt at 81—83° and 85—87° respectively; both have acid (and saponification) number 279 (corresponding with monobasicity), and iodine number 64·4 (corresponding with the formation of a monoiodo-compound).

From the ethereal solution now remaining, 1 per cent. aqueous potassium hydroxide extracts two amorphous acids, the lead salts of which are respectively insoluble and soluble in alcohol. The former of these, *kaurinolic acid*, $C_{17}H_{34}O_2$, melts at 128—130°, has acid (and saponification) number 203 (corresponding with monobasicity), and iodine number 46·9 (corresponding with the formation of a monoiodo-compound). The second, *kauronolic acid*, $C_{12}H_{24}O_2$, melts at 86—89°, has acid (and saponification) number 272 (corresponding with monobasicity) and iodine number 63·15 (corresponding with the formation of a monoiodo-derivative).

When the ethereal solution is freed finally from ether and the residue distilled with steam, an essential oil comes over, boiling at 150—160°, mostly at 156—160°, and with a sp. gr. 0·835 at 15°.

The residue not volatile with steam, *kauorenen*, is an indifferent substance melting at 63—65°; it was not pure, however.

In 100 parts of the drug there are contained:—kauric acid, 1·5; kaurolic acids, 48—50; kaurinolic and kauronolic acids, 20—22; essential oil, 12·5; kauorenen, 12·2; bitter substance, 0·5—1.

C. F. B.

Apiin and Apigenin. By A. CONTI and GIUSEPPE TESTONI (*Gazzetta*, 1901, **31**, i, 73—77).—On hydrolysing crude apiin by means of dilute sulphuric acid, a yellowish powder is obtained which, when acetylated, yields (1) a *triacetyl* derivative which separates from alcohol in slender white needles melting at 215°; this is derived from the

parent substance of the composition $\text{OMe} \cdot \text{C}_{15}\text{H}_6\text{O}_2(\text{OH})_3$, which is probably a flavone derivative; (2) diacetylapienin, and (3) triacetylapienin.

The action of methyl iodide and alcoholic potassium hydroxide yields a *methyl* derivative of apigenin having the composition $\text{C}_{15}\text{H}_6\text{O}_4\text{Me}_4 \cdot \text{OMe}$, and the probable constitution
$$\begin{array}{c} \text{OC} \cdot \text{CMe}_2 - \text{C} - \text{O} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ | \qquad \qquad | \\ \text{MeC} \cdot \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CO} \cdot \text{CH} \end{array}$$
; it separates from alcohol in yellow, acicular crystals melting at 185° , and on oxidation with nitric acid yields anisic acid. T. H. P.

Natal Aloes. By ALEXANDER TSCHIRCH and J. KLAVENESS (*Arch. Pharm.*, 1901, 239, 231—240. Compare Léger, *Bull. Soc. Chim.*, 1900, [iii], 23, 790).—The powdered aloes were macerated with strong alcohol, and the undissolved aloin crystallised from 70 per cent. alcohol; the yield was 15—16 per cent. No substance corresponding with Léger's homonataloin could be detected. Nataloin, $\text{OMe} \cdot \text{C}_{15}\text{H}_{10}\text{O}(\text{OH})_5$, is yellow and crystallises in quadratic tablets or plates; when crystallised from alcohol only, it has no definite melting point, but if crystallised first from acetic acid and then from alcohol, it melts at $202\text{--}204^\circ$; it is anhydrous, although it loses weight when heated in a current of hydrogen gas. It forms a yellowish, amorphous *penta-acetyl* derivative melting at $125\text{--}126^\circ$, together with a small quantity of a crystalline acetyl derivative, which melts at about 240° and contains C 60.6, H 6.15 per cent.; this was regarded by Tilden (*Chem. News*, 1872, 25, 229) as hexa-acetylnataloin, but it is probably derived from a condensation product. Nataloin also forms a *pentabenzoyl* derivative melting at 168° ; it yields oxalic and picric acids when oxidised with nitric acid; when chromic mixture is used, small quantities of fatty acids are formed. When boiled with alcoholic hydrochloric acid, it appears to yield a little emodin.

The resin was precipitated from the alcoholic extract by adding water, and purified by repetition of this treatment (compare Abstr., 1898, i, 599); the mother liquors yielded amorphous *nataloin-red* when neutralised with ammonia and evaporated. The resin was hydrolysed by prolonged boiling with 2 per cent. aqueous potassium carbonate; from the aqueous solution so obtained, sulphuric acid precipitates the resinotannol, whilst ether extracts *p*-coumaric acid, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$, from the liquid remaining. The resin of Natal aloes is thus *nataloresinotannol p-coumarate*. *Nataloresinotannol*, $\text{C}_{22}\text{H}_{18}\text{O}_4(\text{OH})_4$, is a brown powder; it gives a brownish-black coloration with ferric chloride, forms a *tetrabenzoyl* derivative as a light brown powder, and yields oxalic and picric acids when oxidised with nitric acid, and fatty acids and phloroglucinol when fused with potash. C. F. B.

Aniline-Black. By ERNST BÖRNSTEIN (*Ber.*, 1901, 34, 1284—1291).—When aniline-black is oxidised with potassium dichromate, quinone is produced; when it is fused with potassium hydroxide, *p*-diphenylphenylenediamine is obtained, together with a small quantity of a violet substance, which has a coppery lustre and is soluble in alcohol, chloroform or acetone.

Aniline-black may be obtained in good yield, either by Müller's

method (Abstr., 1871, 1098) or by the oxidation of aniline with ammonium persulphate. By extracting the product of the former method with hot toluene, bye-products were obtained which were separated by alcohol into soluble and insoluble portions. The soluble portion yielded yellow plates melting at 223° , red needles melting at 185° , and a third substance which forms dark red crystals and melts at 177° ; all these compounds contain chlorine, but the quantities obtained were too small for further examination. The insoluble portion was found to consist of a mixture of two compounds which were separated by a method depending on a marked difference in their densities. The lighter substance, $C_{24}H_{18}O_2N_3Cl$, crystallises in yellowish, brown needles which have a violet lustre, melts at 337° , and sublimes at a higher temperature without decomposition; when it is warmed with a mixture of sulphuric acid and alcohol, aniline is produced together with a brown substance, which crystallises in small, four-sided tablets and melts at 277° ; if it is distilled with zinc dust, it yields aniline and a substance which crystallises in microscopic red needles. The heavier substance, $C_{30}H_{21}O_2N_4Cl_3$, crystallises in dark brown leaflets and melts at 286° ; when heated with alcoholic sulphuric acid, aniline is produced together with a yellow, crystalline substance. E. G.

2-Acetylfurfuran from Wood-Tar and its Synthesis. By LOUIS BOUVEAULT (*Ber.*, 1901, 34, 1072—1073. Compare Abstr., 1899, i, 120).—The synthesis described by the author has been repeated by Sandelin (Abstr., 1900, i, 305).

2-Acetylfurfuran is best obtained from wood-tar by treatment with 30 per cent. sulphuric acid. The portion dissolved by acid of this strength is treated with sodium hydrogen sulphite, and the insoluble part distilled, when the 2-acetylfurfuran passes over between 65° and 70° . The benzoyl derivative of the oxime forms colourless crystals and melts at $97-98^{\circ}$. The semicarbazone crystallises in yellow needles melting at 148° . A. H.

Nomenclature of Coumarone Derivatives. By RICHARD STOERMER (*Ber.*, 1901, 34, 1148—1150. Compare Abstr., 1900, i, 650).—Polemical. A reply to Simonis (*Ber.*, 1901, 34, 781).

J. J. S.

Derivatives of 1:4-Benzopyranol, the Mother Substance of a New Class of Colouring Matters. By CARL BULOW and HERMANN WAGNER (*Ber.*, 1901, 34, 1189—1210).—Acetylacetone and other 1:3-diketones and aldehyd ketones readily condense with phenols to form derivatives of 1:4-benzopyranol (1:4-chromanol), $HC:CH \cdot C \cdot O \text{---} CH$, the compound derived from resorcinol and acetylacetone being 7-hydroxyanthydro-2:4-dimethyl-1:4-benzopyranol, $HC:CH \cdot C \cdot CH(OH) \cdot CH$, $OH \cdot C_6H_3 \text{---} O \text{---} C(CH_3) \cdot CH$.

These substances, which are closely related to the derivatives of flavone, have basic properties and their hydrochlorides act as dyes. The constitution follows from the mode of preparation and from the

nature of the products obtained by the action of 10 per cent. aqueous potash.

7-Hydroxyanhydro-2:4-dimethyl-1:4-benzopyranol is obtained by the condensation of resorcinol with acetylacetone in acetic acid solution in presence of hydrogen chloride, and forms an amorphous, orange-coloured mass. The *hydrochloride*, $C_{11}H_{10}O_2 \cdot HCl$, crystallises with $1H_2O$ in straw-yellow coloured prisms and is decomposed by water. It becomes dark coloured at 160° and black at 200° . This salt probably has the constitution $OH \cdot C_6H_3 \begin{smallmatrix} \diagup O \\ \diagdown C(:CH_2) \cdot \end{smallmatrix} \begin{smallmatrix} \diagup CHMe \\ \diagdown CHCl \end{smallmatrix}$. The solution in sulphuric acid shows an intense green fluorescence.

The colour base is decomposed by boiling aqueous potash, yielding resacetophenone and acetone, and the constitution which has been assigned to it is thus confirmed. The *picrate*, $C_{11}H_{10}O_2 \cdot C_6H_3O_7N_3$, crystallises in greenish-yellow, rhombic tablets. Acetic anhydride in presence of sodium acetate and acetic acid yields an *acetyl* derivative, $OAc \cdot C_6H_3 \cdot C_5H_6O$, which is a faintly yellow powder, and softens and becomes resinous at $150-155^\circ$. A methyl derivative could not be prepared. 5:7-Dihydroxyanhydro-2:4-dimethyl-1:4-benzopyranol,

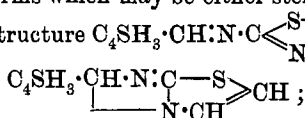
$C_6H_2(OH)_2 \begin{smallmatrix} \diagup O \\ \diagdown C(:CH_2) \cdot \end{smallmatrix} \begin{smallmatrix} \diagup CHMe \\ \diagdown CH \end{smallmatrix}$, is prepared from acetylacetone and phloroglucinol, and forms a yellow, microcrystalline powder containing $1H_2O$, which is lost at 115° . Aqueous potash converts it into acetone, phloroglucinol, and acetic acid, the latter two substances being probably products of the secondary decomposition of 2:4:6-trihydroxyacetophenone. The *hydrochloride* forms a lemon-yellow, crystalline powder which blackens at 250° . The solution in sulphuric acid shows no fluorescence. The *picrate* crystallises in small, yellow prisms and the *acetyl* derivative is a yellowish-white, amorphous powder and softens at $145-155^\circ$.

7:8-Dihydroxyanhydro-2:4-dimethyl-1:4-benzopyranol is obtained from acetylacetone and pyrogallol and is a violet-red, amorphous powder which decomposes above 150° ; when treated with aqueous potash, it yields gallacetophenone and acetone. The *hydrochloride* forms dark orange crystals containing $1H_2O$, decomposes above 200° , and forms a non-fluorescent solution in sulphuric acid. The *picrate* crystallises in fascicular groups of slender needles, and the *acetyl* derivative is a yellowish-white, amorphous powder. A. H.

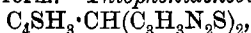
Phenanthroxazine. By FRANCIS JAPP and WILLIAM B. DAVIDSON (*Ber.*, 1901, 34, 806).—Phenanthroxazine (Bamberger and Grob, this vol., i, 280) is identical with the compound $C_{28}H_{17}ON$, obtained by the authors (*Trans.*, 1895, 67, 47). C. F. B.

Anils of Thiophenalddehyde. By ARTHUR HANTZSCH and RUDOLF WIRZ (*Ber.*, 1901, 34, 841-847).—Thiophenalddehyde and aniline yield on condensation a yellow oil which was not analysed. *Thiophenidene-p-toluidine*, $C_4SH_8 \cdot CH:N \cdot C_6H_4Me$, obtained by warming the aldehyde with the base, crystallises from alcohol in yellow prisms and melts at 36° . *Thiophenidene-p-bromoaniline* forms bright yellow leaflets and melts at 90° . The foregoing compounds exist only in one form,

which has probably the configuration $\text{C}_4\text{SH}_3 \cdot \text{C} \begin{smallmatrix} \text{H} \\ | \\ \text{N} \end{smallmatrix} \text{Ar}$, since the hydrochlorides are stable in contact with water and in this respect resemble the stable hydrochlorides of the *syn*-aldoximes, and differ from the unstable hydrochlorides of the *anti*-aldoximes and of the benzaldehyde-anils, which have the configuration $\text{Ph} \cdot \text{C} \begin{smallmatrix} \text{H} \\ | \\ \text{N} \end{smallmatrix} \text{Ar}$. *Thiophenideneaminothiazole* exists in two forms which may be either stereoisomerides or tautomerides having the structure $\text{C}_4\text{SH}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{C} \begin{smallmatrix} \text{S} \cdot \text{CH} \\ | \quad | \\ \text{N} \cdot \text{CH} \end{smallmatrix}$ and



the α -form, obtained on warming thiophenylaldehyde with aminothiazole (1 mol.), crystallises from alcohol in bright yellow leaflets, melts at 109° , and is converted at this temperature, when heated in nitrogen, into the β -form melting at $47\text{--}48^\circ$, which again changes, either on recrystallisation from alcohol or after 7 or 8 days at the ordinary temperature, into the α -form. *Thiophenidenebisaminothiazole*,



the product of the action of thiophenylaldehyde with 2 mols. of aminothiazole, melts at 117° with decomposition into its components; when dissolved in *p*-toluidine, thiophenidene-*p*-toluidine is formed along with 2 mols. of aminothiazole, as shown by determinations of the molecular weight by the cryoscopic and ebullioscopic methods. Benzylidene-bisaminothiazole (this vol., i, 378) is decomposed similarly by *p*-toluidine.

W. A. D.

Action of Halogens and Carbon Disulphide on Sodium-Methylene Compounds. By G. WENZEL (*Ber.*, 1901, 34, 1043—1050).—The compounds obtained by the author (Abstr., 1900, i, 536) by the action of bromine and carbon disulphide on ethyl sodiomalonate and ethyl sodiocyanoacetate have the composition $\text{C}_{16}\text{H}_{20}\text{O}_8\text{S}_3$ and $\text{C}_{12}\text{H}_{10}\text{O}_4\text{N}_2\text{S}_3$ respectively, and not $\text{C}_{16}\text{H}_{22}\text{O}_8\text{S}_3$ and $\text{C}_{12}\text{H}_{12}\text{O}_4\text{N}_2\text{S}_3$, as at first supposed. The former compound is *ethyl dithiotetrahydrothiophentetracarboxylate*, $\text{S} \begin{smallmatrix} \text{CS} \cdot \text{C}(\text{CO}_2\text{Et})_2 \\ | \\ \text{CS} \cdot \text{C}(\text{CO}_2\text{Et})_2 \end{smallmatrix}$, whilst the latter is the

diethyl ester of the corresponding dinitrile, $\text{S} \begin{smallmatrix} \text{CS} \cdot \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et} \\ | \\ \text{CS} \cdot \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et} \end{smallmatrix}$.

When bromine or iodine is added to ethyl sodiocyanoacetate suspended in cold carbon disulphide, Errera and Perciabosco's ethyl tricyanotrimethylenetetracarboxylate (this vol., i, 18) is produced; if, however, the carbon disulphide is heated to boiling before the addition of the halogen, the diethyl ester of the dinitrile of dithiotetrahydrothiophentetracarboxylic acid is obtained. If the carbon disulphide is heated in the preparation of the tetraethyl ester, the yield of this compound is

increased, and *ethyl dithiotetramethylenetetracarboxylate*, $\text{CS} \cdot \text{C}(\text{CO}_2\text{Et})_2 \begin{smallmatrix} \text{CS} \cdot \text{C}(\text{CO}_2\text{Et})_2 \\ | \\ \text{CS} \cdot \text{C}(\text{CO}_2\text{Et})_2 \end{smallmatrix}$, is simultaneously formed, which crystallises in colourless, feathery needles, and melts at $179\text{--}180^\circ$; it is identical with the ethyl thio-

carbonylmalonate obtained by Bergreen (Abstr., 1888, 445) by the action of thiocarbonyl chloride on ethyl sodiomalonate. *Dithiotetramethylene-tetracarboxylic acid* crystallises in white needles, decomposes at 310° , and cannot be recrystallised without change; it is also produced by the hydrolysis of ethyl dithiotetrahydrothiophentetracarboxylate; its *potassium, sodium, ammonium, barium, and calcium* salts were prepared,

Ethyl dithiobutanetetracarboxylate, $\text{CH}(\text{CO}_2\text{Et})_2 \cdot \text{CS} \cdot \text{CS} \cdot \text{CH}(\text{CO}_2\text{Et})_2$ obtained by reduction of ethyl dithiotetramethylenetetracarboxylate with zinc dust and acetic acid, crystallises in long, colourless needles, melts at 103° , and is soluble in acetone or dilute alcoholic alkali.

When the diethyl ester of the dinitrile of dithiotetrahydrothiophentetracarboxylic acid is heated with bromine and water, the *dibromo-additive product*, $\text{C}_4\text{SBr}_2\text{S}_2(\text{CN})_2(\text{CO}_2\text{Et})_2$, is obtained as a yellow oil; it crystallises from alcohol in yellow, prismatic needles, melts at $95-96^{\circ}$, and is not affected when heated with silver at $200-250^{\circ}$.

If an alcoholic solution of ethyl dithiotetramethylenetetracarboxylate is heated with phenylhydrazine, hydrogen sulphide is produced, and on cooling, the *tetraphenylhydrazine* salt separates in lustrous leaflets.

Dithiodiphenyltetramethylenedinitrile, $\begin{array}{c} \text{CS} \cdot \text{CPh} \cdot \text{CN} \\ \text{CS} \cdot \text{CPh} \cdot \text{CN} \end{array}$ obtained by the action of carbon disulphide and bromine on sodiobenzyl cyanide, crystallises from dilute acetone in long, yellow needles and melts at 174° .

Dithiotetra-acetyltetramethylene, $\begin{array}{c} \text{CS} \cdot \text{CAc}_3 \\ \text{CS} \cdot \text{CAc}_3 \end{array}$, produced in small quantity by the action of carbon disulphide and bromine on sodium acetylacetone, crystallises from glacial acetic acid in golden-yellow prisms, and melts at 230° ; it may be obtained in better yield from sodium acetylacetone and thiocarbonyl chloride. E. G.

Oxidation of Arginine. I. By ELOPHE BÉNECH and FR. KUTSCHER (*Zeit. physiol. Chem.*, 1901, **32**, 278—280).—On oxidation with barium permanganate, arginine yields guanidine, which is best isolated in the form of its picrate. The second product of oxidation is undoubtedly α -amino-*n*-valeric acid, and arginine is thus guanidine- α -aminovaleric acid. J. J. S.

Tautocinchonine. By FRIEDRICH LANGER (*Monatsh.*, 1901, **22**, 151—156).—*alloCinchonine* is the chief product formed on removing, by means of alcoholic silver nitrate, hydrogen bromide from trihydrobromocinchonine prepared either from the commercial or carefully purified cinchonine dihydrobromide. The commercial product yielded also a base with a higher melting point (261°), which is apparently identical with the tautocinchonine obtained by von Lowenhaupt (Abstr., 1899, i, 176). This base is, however, a mixture from which some 40 per cent. of cinchotine can be isolated. With alcoholic potash, trihydrobromocinchonine similarly yields chiefly *allocinchonine*, together with some δ -cinchonine and α -isocinchonine. K. J. P. O.

Bases Analogous to Nicheine from Cinchonine. By FRIEDRICH LANGER (*Monatsh.*, 1901, **22**, 157—170).— δ -Cinchonine hydrochloride

prepared from trihydrobromocinchonine, by von Lowenhaupt's method (Abstr., 1899, i, 176) is shown to have the formula $C_{18}H_{22}ON_2 \cdot HCl, 1\frac{1}{2}H_2O$. From this fact and from the composition of other derivatives, the base must be represented by the formula $C_{18}H_{22}ON_2$, and not $C_{19}H_{23}ON_2$ as hitherto supposed. The base melts at $141\cdot5$ — 142° and has $[\alpha]_D + 139\cdot45^\circ$ at 20° . δ -Cinchonine thus bears the same relation to cinchonine as nicine does to quinine.

The acid δ -cinchonine dihydriodide, $C_{18}H_{22}ON_2 \cdot 2HI$, forms plates melting at 232° . By the action of concentrated hydriodic acid the latter forms an *additive product*, $C_{18}H_{22}ON_2 \cdot 3HI$, which crystallises in needles melting at 243 — 244° . The base, hydriodo- δ -cinchonine is converted into δ -cinchonine by the action of alcoholic silver nitrate.

Nitroso- δ -cinchonine, $C_{18}H_{21}ON_2 \cdot NO$, prepared from δ -cinchonine hydrochloride by the action of sodium nitrite, forms an amorphous powder which gives Liebermann's reaction.

Hydriodocinchonine, when treated with alcoholic silver nitrate, yields a base, which appears to be identical with δ -cinchonine.

Hydrochlorocinchonine, under the action of alcoholic potash, is converted into a *base*, $C_{19}H_{23}ON_2$, and α -isocinchonine. The former melts at $170\cdot5$ — 171° , and has $[\alpha]_D - 7\cdot0^\circ$ at 20° ; the *hydrochloride* crystallises in leaves.

K. J. P. O.

Transformation of Cinchonine by means of Sulphuric Acid. By ZDENKO H. SKRAUP (*Monatsh.*, 1901, 22, 171—190. Compare Abstr., 1899, i, 961).—Sulphuric acid is far less effective in producing the transformation of cinchonine into α - and β -isocinchonine than hydrogen chloride, bromide, or iodide. The change, however, proceeds with measurable velocity when concentrations from $19\cdot5$ to $30\cdot5$ *N* sulphuric acid are used.

The changes, which occur may be represented as follows: cinchonine \rightarrow α -isocinchonine \rightleftharpoons β -isocinchonine \rightleftharpoons allocinchonine. Of these the two latter are to a certain extent reversible. Concomitantly with the transformation of any given alkaloid, sulphonation of that alkaloid or the formation of a sulphuric acid additive product is effected. The change of cinchonine into α -isocinchonine takes place with so much greater velocity than the change of the latter into β -isocinchonine, that practically the whole of the cinchonine disappears before any β -isocinchonine is formed. In the action of sulphuric acid on cinchonine, the proportion of the alkaloid converted into α -isocinchonine is approximately three times that sulphonated. An account is given in the paper of the quantitative experiments from which these results are deduced, and of the methods of estimating cinchonine, and α - and β isocinchonine in mixtures containing the three alkaloids.

The sulphonic acid derivatives were not obtained in a pure state, but a *cupric* salt, $C_{19}H_{22}ON_2 \cdot SO_4Cu$ was isolated.

K. J. P. O.

alloCinchonine. By OTTOKAR JOSEF HLAVNIČKA (*Monatsh.*, 1901, 22, 191—205).—*alloCinchonine*, prepared by the action of silver nitrate on hydriodocinchonine, yields a *dihydriodide* melting at 236 — 239° and crystallising in pale yellow prisms, and a normal *sulphate*, $C_{19}H_{22}ON_2 \cdot H_2SO_4 \cdot 3H_2O$, crystallising in large prisms.

By the action of concentrated hydriodic acid on *allocinchonine*, the dihydriodide and an *additive* compound, $C_{19}H_{25}ON_2I_3$, melting at 227° are formed. By the action of alcoholic potash on trihydriodo-*allocinchonine*, α -*isocinchonine* and *allocinchonine* are obtained. With phenylhydrazine, this alkaloid does not react.

Phenylcarbimide gives a *derivative*, $C_{19}H_{21}ON_2 \cdot CO \cdot NPh$, which forms colourless prisms melting at 191.5 — 192° , and is decomposed by hydrochloric acid with the production of aniline. In this reaction with phenylcarbimide, *allocinchonine* resembles cinchonine, and is distinguished from α - and β -*isocinchonine*.

On heating the normal sulphate previously mentioned at 140° , a tarry mass is produced from which a base can be obtained. The *oxalate* of this base, $(C_{19}H_{22}ON_2)_2 \cdot C_2H_2O_4 \cdot 13H_2O$, forms silky needles melting at 170° . The base, prepared from the oxalate, reacts with phenylhydrazine, yielding a *phenylhydrazone*, $C_{19}H_{22}ON_2 \cdot N_2HPh$, a red, brittle solid melting at about 94 — 96° . By heating with 63 per cent. sulphuric acid, *allocinchonine* is chiefly converted into β -*isocinchonine*, together with a small amount of a sulphonic acid.

K. J. P. O.

Bases in Mandragora Roots. By HERMANN THOMS and M. WENTZEL (*Ber.*, 1901, **34**, 1023—1026. Compare *Abstr.*, 1898, i, 708).—Besides the alkaloid hyoscyamine, the authors have now succeeded in isolating another alkaloid, scopolamine, from mandragora roots. The roots in a fine state of division are extracted with alcoholic tartaric acid; the acid extract, after neutralisation with sodium hydrogen carbonate, is thoroughly extracted with ether, by which means the whole of the scopolamine, which is not strongly basic, together with a small amount of the more strongly basic hyoscyamine, pass into the ether. By fractional crystallisation of the aurichlorides, pure scopolamine aurichloride is obtained, melting at 204° . The hydrobromide obtained by a similar process is shown to be identical in optical activity, &c., with that prepared by Schmidt (*Abstr.*, 1892, 1255).

K. J. P. O.

Morphidine. By EDUARD VONGERICHTEN (*Ber.*, 1901, **34**, 1162—1164. Compare this vol., i, 767).—The substance, obtained in very small quantity, together with phenanthrene on distilling morphine with zinc dust, and previously described as morphidine (*Ber.*, 1901, **34**, 767), is in reality a mixture of two bases. The two bases appear to be practically identical in properties with the exception that the methiodide of one of them is readily decomposed by sodium hydroxide, whilst the other is not. To the *platinichlorides*, the formulæ $(C_{17}H_{16}N)_2PtCl_6$ and $(C_{17}H_{14}N)_2PtCl_6$, are ascribed respectively.

J. J. S.

Alkaloids of Peganum Harmala. By OTTO FISCHER (*Chem. Centr.*, 1901, i, 957—959; from *Festschr. zum 80 Geburtstag des Prinzregenten Luitpold*, Erlangen, 1901. Compare *Abstr.*, 1885, 821; 1889, 730, and 1898, i, 164).—Harmalol has been isolated from the seeds of *Peganum harmala*, and is identical with the product obtained by the action of concentrated hydrochloric acid on harmaline; the green

fluorescence of its aqueous solution is almost completely destroyed by acids or alkalis. Harmine melts at 257—259°. Harminic acid is an ortho-dicarboxylic acid, but on titration behaves like a monobasic acid, one carboxyl group being combined as in a salt. Apoharmine is decomposed by potassium permanganate, forming ammonia and oxalic acid; its nitro-derivative has both acid and basic properties (compare the nitroiminazoles of Bamberger and Berlé). The *aurichloride* crystallises in orange-yellow needles concentrically arranged. Harmol cannot be directly reduced by the action of hydriodic acid or of zinc dust, but the oxygen may be eliminated indirectly by means of the amino-derivative.

Aminoharman, $C_{12}H_{11}N_3$, prepared by the action of ammonio-zinc chloride and ammonium chloride on harmol at 250°, crystallises from water in flat needles or leaflets, has a silvery lustre, sinters at 292°, melts at 298°, sublimes with partial decomposition, and is easily soluble in alcohol. The solutions of the salts show a blue fluorescence. The *hydrochloride* crystallises in colourless prisms, and is slightly soluble in water; the *nitrate* and *sulphate* were also prepared. *Harman*, $C_{12}H_{10}N_2$, obtained by diazotising the amino-derivative, resembles harmine, and separates in leaflets or flat needles; it crystallises from benzene in small, stout crystals, melts at 230°, sublimes with partial decomposition, forming a sublimate which crystallises in needles, and is readily soluble in ethyl or methyl alcohol. Its solution in concentrated sulphuric acid has a faint blue fluorescence, whilst the solutions of its salts show a strong blue fluorescence. The *platinichloride*, $(C_{12}H_{10}N_2)_2 \cdot H_2PtCl_6 \cdot \frac{1}{2}H_2O$, crystallises in pale yellow needles and is slightly soluble in water; the *aurichloride* separating in matted, orange needles and the *mercurichloride* was also prepared.

Harmaline crystallises from alcohol or benzene in large, colourless crystals which, in thicker layers, appear yellow. Its solution in concentrated sulphuric acid is intensely yellow but not fluorescent, whilst the alcoholic solutions of the yellow salts have a green fluorescence. By the action of hydrochloric acid on a boiling solution of acetyl-harmaline in alcohol, the solution becomes brown, green, and finally dirty blue, and from the product ammonia precipitates a strong base, $C_{15}H_{18}O_3N_2$, in almost colourless needles or leaflets; it separates from water in yellow crystals, melts at 164—165°, is easily soluble in hot water, and forms yellow solutions in acids. The *platinichloride*, $(C_{15}H_{18}O_3N_2)_2 \cdot H_2PtCl_6$, crystallises in lustrous, brown needles, and decomposes at 210°. The *aurichloride* is difficult to obtain in a crystalline form. The *mercurichloride* was also prepared. The base is only reconverted into harmaline by prolonged boiling with alcoholic potash, and by the action of hydrochloric acid at 150—160° it forms harmalol. When harmaline is boiled with nitric acid of sp. gr. 1.48, nitroanisic acid $[OMe:NO_2:CO_2H = 1:2:4]$ is formed together with harminic acid. The former acid is derived from methoxynitrophthalic acid by elimination of carbon dioxide. The harmaline alkaloids must therefore contain a complex, $OMe \cdot C_6H_3(C-)C$, in which $OMe:C:C = 1:3:4$ or $1:4:5$.

The physiological effect of these alkaloids is to reduce the temperature.

A summary of all the known derivatives of this group is given in the original paper.

E. W. W.

Acid Chlorides of the Pyridine Series. By HANS MEYER (*Monatsh.*, 1901, 22, 109—117).—The pyridinecarboxylic acids are converted into the chlorides by gently heating the acid with thionyl chloride in a sealed tube.

Picolinic chloride, $C_5NH_4 \cdot COCl$, forms small, colourless needles melting at 220° which sublime without decomposing. With water, it yields the hydrochloride of picolinic acid, and with alcohol the ethyl ester.

Nicotinic chloride, $C_6NH_4 \cdot COCl$, a white powder, melts and decomposes at 245° ; it combines with hydrogen chloride to form the hydrochloride.

isoNicotinic chloride, $C_6NH_4 \cdot COCl$, forms white needles melting and decomposing at 270° , and melting at 240 — 245° in a closed capillary tube.

Cinchonic acid reacts very readily with thionyl chloride, forming the *hydrochloride* of the chloride, $C_9NH_6 \cdot COCl, HCl$, which crystallises in faintly yellow needles melting at 170° . *Cinchonic chloride* is obtained as yellow needles by allowing the hydrochloride to stand over sodium hydroxide. It melts at 109° and distils at 210° . *Methyl cinchonate*, prepared from the acid chloride by the action of methyl alcohol, melts at 24° .

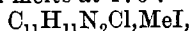
With thionyl chloride, quinolinic and cinchomeronic acids yield only the anhydrides. K. J. P. O.

Constitutional Formula of Fischer's Base. By KARL BRUNNER (*Gazzetta*, 1901, 31, i, 181—183).—A reply to Plancher, who claims priority in putting forward the constitutional formula of Fischer's base (1 : 3 : 3-trimethyl-2-methyleneindoline). T. H. P.

Chloro-*m*-phenylenediamine. By PAUL COHN (*Monatsh.*, 1901, 22, 118—222. Compare *Abstr.*, 1900, i, 458).—By the reduction of chlorodinitrobenzene (1 : 3 : 5) with stannous chloride, 5-chloro-*m*-phenylenediamine is prepared; it forms prisms melting at 105 — 106° , which belong to the rhombic system [$a : b : c = 1 : 0.7115 : 0.4709$]. The *hydrochloride*, *sulphate*, and *platinichloride* all crystallise well; the first named readily darkens in the air. The *diacetyl* derivative forms light brown needles, which do not melt at 300° ; the *dibenzoyl* derivative crystallises in needles melting at 254 — 255° .

With benzenediazonium salts, the base gives an azo-dye, and by Sandmeyer's reaction it is easily converted into 1 : 3 : 5-trichlorobenzene. K. J. P. O.

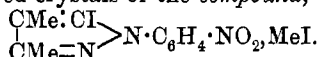
Some 5-Halogen-phenylalkylpyrazoles. By AUGUST MICHAELIS, U. VOSS and MAX GREISS (*Ber.*, 1901, 34, 1300—1308).—5-Chloro-1-phenyl-3 : 4-dimethylpyrazole (Michaelis and Röhmer, *Abstr.*, 1899, i, 233) is a colourless liquid of remarkable odour, which boils at 281° and forms thick, colourless crystals melting at 26° ; its *hydrochloride* sublimes on heating and is decomposed by water; the *platinichloride* crystallises with $2H_2O$, and melts at 176° . The *methiodide*,



crystallises in white leaflets and melts at 235° . The corresponding *methochloride* forms hygroscopic crystals; its *platinichloride* ($C_{11}H_{11}N_2Cl, MeCl$) $_2, PtCl_4$, crystallises in yellow needles. When the

methiodide or methochloride is treated with alcoholic potassium hydroxide, it is converted into 1-phenyl-2:3:4-trimethylpyrazolone. On reduction of chlorophenyldimethylpyrazole with hydriodic acid, phenyldimethylpyrazole is obtained, whilst by the action of sodium on an alcoholic solution, phenyldimethylpyrazoline is produced. The

p-nitro-derivative, $\begin{array}{c} \text{CMe}:\text{CCl} \\ | \\ \text{CMe}=\text{N} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, crystallises in white needles and melts at 140° ; when heated at 110° with excess of methyl iodide, it yields yellowish-red crystals of the compound,



The corresponding amino-derivative, $\text{C}_3\text{N}_2\text{Me}_3\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, crystallises in white leaflets and melts at 75 – 78° . Chlorodinitrophenyldimethylpyrazole, $\text{C}_3\text{N}_2\text{Me}_2\text{Cl} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, forms lustrous crystals and melts at 121° ; the corresponding diamino-derivative could not be obtained.

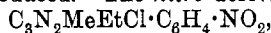
5-Chloro-1-phenyl-3-methylpyrazole-4-carboxylic acid, obtained by the oxidation of chlorophenyldimethylpyrazole with chromic acid, crystallises in plates, melts at 228 – 229° , and dissolves easily in ether or glacial acetic acid; it does not combine with methyl iodide. When this acid is heated in a closed tube at 230 – 240° , carbon dioxide and 5-chloro-1-phenyl-3-methylpyrazole are produced. The acid chloride melts at 85° , and by the action of water is readily converted into the acid. The amide melts at 183° , and dissolves readily in alcohol and sparingly in ether.

5-Bromo-1-phenyl-3:4-dimethylpyrazole, $\begin{array}{c} \text{CMe}:\text{CBr} \\ | \\ \text{CMe}=\text{N} \end{array} > \text{NPh}$, obtained by heating the corresponding chloropyrazole with ethyl bromide at 210° in a sealed tube, forms transparent crystals, melts at 51° , and boils at 210 – 220° under 100 mm. and at 295° under atmospheric pressure. The methobromide, $\text{C}_{11}\text{H}_{11}\text{N}_2\text{Br} \cdot \text{MeBr}$, crystallises in white leaflets and melts and decomposes at 230° .

When chlorophenyldimethylpyrazole is heated with ethyl iodide, the ethiodide of the corresponding iodopyrazole, $\text{C}_{11}\text{H}_{11}\text{N}_2\text{I} \cdot \text{EtI}$, is produced, which crystallises in white, pearly leaflets and melts and decomposes at 222 – 223° . The ethochloride, $\text{C}_{11}\text{H}_{11}\text{N}_2\text{I} \cdot \text{EtCl} \cdot 4\text{H}_2\text{O}$, obtained by shaking a hot aqueous solution of the ethiodide with silver chloride, crystallises in small, white prisms and melts at 85° ; the anhydrous substance melts at 190° . When the ethochloride is distilled under 25–30 mm. pressure, it yields ethyl chloride and 5-iodo-1-phenyl-3:4-dimethylpyrazole, which forms pale yellow crystals, melts at 78° , and is soluble in ether or alcohol. The ethiodide of 5-iodo-1-phenyl-3-methylpyrazole (Michaelis and Pasternack, Abstr., 1899, ii, 942) can be similarly converted into the ethochloride, and by distilling this in a vacuum, the pyrazole itself is obtained as an almost colourless oil.

5-Chloro-1-phenyl-3-methyl-4-ethylpyrazole, $\begin{array}{c} \text{CEt}:\text{CCl} \\ | \\ \text{CMe}=\text{N} \end{array} > \text{NPh}$, obtained by the action of phosphorus oxychloride on phenylmethylethylpyrazolone, forms white crystals, melts at 40° , and boils at 175° under 50 mm. and at 285° under atmospheric pressure; its platinumchloride forms large, red crystals containing $1\text{H}_2\text{O}$, and melts at 173° . The methiodide

melts at 176° , the *methobromide* at 197° , and the *methochloride* at 162° ; when these compounds are treated with alcoholic potassium hydroxide, 4-ethylantipyrine is produced. The *nitro-derivative*,



crystallises in white needles, melts at 71° , and on reduction is converted into the *amino-derivative* melting at 107° ; the *dinitro-derivative* melts at 138° . When the pyrazole is oxidised with chromic acid, it is converted into 5-chloro-1-phenyl-3-methylpyrazole-4-carboxylic acid.

The *pyrazoline*, $\begin{array}{c} \text{CHEt} \cdot \text{CH}_2 \\ | \\ \text{CMe} = \text{N} \end{array} \text{NPh}$, obtained by the action of sodium on an alcoholic solution of the pyrazole, is a pale yellow liquid which boils at 294° ; its *nitro-derivative* crystallises in yellow needles and melts at 121° .

1-Phenyl-4-benzyl-3-methylpyrazolone, first obtained by Walker (Abstr., 1894, i, 476) by the action of benzyl chloride on phenyl-methylpyrazolone, may also be prepared by the condensation of ethyl benzylacetoacetate with phenylhydrazine; when heated with phosphorus oxychloride, it is converted into 5-chloro-1-phenyl-4-benzyl-

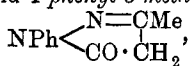
3-methylpyrazole, $\begin{array}{c} \text{C} \cdot \text{C}_7\text{H}_7 \cdot \text{CCl} \\ | \\ \text{CMe} = \text{N} \end{array} \text{NPh}$, which crystallises in colourless prisms and melts at 50° . The *methiodide* of the last-mentioned compound melts at 167° , and is converted by alcoholic potassium hydroxide

into *benzylantipyrine*, $\begin{array}{c} \text{C}_7\text{H}_7 \cdot \text{C} = \text{C} \\ | \quad | \\ \text{O} \quad \text{O} \\ | \quad | \\ \text{CMe} : \text{NMe} \end{array} \text{NPh}$, which crystallises in

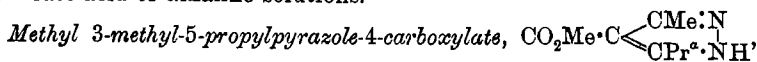
needles and melts at 70° ; its *hydrochloride* melts at 167° . The *nitro-derivative* of the chloropyrazole melts at 128° , and on reduction yields the *amino-derivative* which crystallises in white leaflets and melts at 100° . E. G.

Action of Phenylhydrazine and Hydrazine on the Two Isomeric Methyl Butyrylacetates. By A. BONGERT (*Compt. rend.*, 1901, 132, 973—975. Compare this vol., i, 311).—Methyl-butyrylacetate (C-ester) and phenylhydrazine interact, giving rise to acetylphenylhydrazine, *phenylpropylpyrazolone*, $\text{C}_{12}\text{H}_{14}\text{ON}_2$, and a *bispyrazolone*, $(\text{C}_{12}\text{H}_{13}\text{ON}_2)_2$; the former of these new compounds melts at 108° and boils at about 200° under 10 mm. pressure; the latter, which is insoluble in neutral solvents, crystallises in needles from glacial acetic acid and melts at 346° ; it readily dissolves in dilute acids and alkaline solutions, and develops with ferric chloride an intense blue coloration.

With phenylhydrazine, the O-ester (methyl butyryloxymethacrylate) yields methyl alcohol, *butyrylphenylhydrazine*, crystallising in silky needles melting at 102° and 1-phenyl-3-methylpyrazolone,



a compound which melts at 125° and is readily soluble in ether, alcohol, or dilute acid or alkaline solutions.



produced by mixing in alcoholic solutions equal mols. of hydrazine and methyl butyrylacetacetate (C-ester), is a viscid oil boiling at 179° under 10 mm. pressure; it yields a crystalline derivative with hydrochloric acid which is readily decomposed by hot water or cold dilute alkaline solutions.

The acid obtained by hydrolysing the preceding ester with 20 per cent. potassium hydroxide separates from ether or alcohol in white crystals and melts at 226° ; when heated at higher temperatures, it evolves carbon dioxide and yields an oil having a pungent odour which is in all probability 3-methyl-5-propylpyrazole.

3-Methyl-5-pyrazolone, $\text{NH} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, melting at $215-216^{\circ}$, is formed together with butyrylhydrazine and methyl alcohol by the action of hydrazine on the O-ester.

Benzylidenebutrylhydrazone, $\text{C}_6\text{H}_7 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CHPh}$, produced by mixing together benzaldehyde and butyrylhydrazine in the presence of a solution of an alkali hydroxide, crystallises in silky needles and melts at 96° .

The butyrylhydrazone of acetone melting at 83° results from the action of butyrylhydrazine on acetone; it is very soluble in the ordinary organic solvents with the exception of light petroleum.

G. T. M.

Condensation of Barbituric Acid with Aldehydes. By MAX CONRAD and H. REINBACH (*Ber.*, 1901, **34**, 1339—1344).—Barbituric acid readily condenses with aldehydes in the absence of any condensing agent.

Benzylidenobarbituric acid, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{OC} \end{smallmatrix} \text{C} \cdot \text{CHPh}$, prepared by heating equal quantities of barbituric acid in aqueous solution and benzaldehyde for 1 or 2 hours on the water-bath, forms colourless prisms from boiling acetic acid which melt at 256° . On treatment with cold aqueous sodium hydroxide or ammonia, it decomposes with the formation of benzaldehyde. Benzylbarbituric acid is obtained on reduction with zinc dust and acetic acid.

o-Nitrobenzylidenobarbituric acid, $\text{C}_{11}\text{H}_7\text{O}_5\text{N}_2$, forms crystals which become coloured at 240° and melt and decompose at $250-252^{\circ}$. With aqueous ammonia, it yields a yellow additive product, $\text{C}_{11}\text{H}_{10}\text{O}_5\text{N}_4$.

o-Aminobenzaldehyde and barbituric acid give a compound, $\text{C}_{11}\text{H}_7\text{O}_2\text{N}_3$, which is formed by the elimination of water from the *o*-aminobenzylidenobarbituric acid first produced. It decomposes above 280° without melting and can be sublimed. It exhibits both acid and basic properties, and forms a hydrochloride, $\text{C}_{11}\text{H}_7\text{O}_2\text{N}_3 \cdot \text{HCl}$, and a sodium salt, $\text{C}_{11}\text{H}_6\text{O}_2\text{N}_3\text{Na} \cdot 2\text{H}_2\text{O}$, as a yellow precipitate. On heating the latter at 200° , ammonia is evolved; when the residue is treated with hydrochloric acid, carbon dioxide is given off, and carbostyryl-3-carboxylic acid is obtained.

Cinnamylidenobarbituric acid, $\text{CHPh} \cdot \text{CH} \cdot \text{CH} \cdot \text{C} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CO}$, prepared from cinnamaldehyde and barbituric acid, crystallises in lemon-yellow prisms melting and decomposing at $226-228^{\circ}$.

Furfurylidenebarbituric acid, $C_4OH_3 \cdot CH : C \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > CO$, forms an insoluble yellow powder decomposing above 280° .

Salicylidene-bis-barbituric acid, $OH \cdot C_6H_4 \cdot CH \left(CH \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > CO \right)_2$, obtained from salicylaldehyde and barbituric acid, is a white, crystalline powder which darkens at 225° and melts and decomposes at 260° .
K. J. P. O.

Indazole. By EMIL FISCHER and OTTO SEUFFERT (*Ber.*, 1901, 34, 795—798).—When *o*-hydrazinobenzoic acid, $NH_2 \cdot NH \cdot C_6H_4 \cdot CO_2H$, or more conveniently its hydrochloride, is boiled under atmospheric pressure with 6—7 times its weight of phosphorus oxychloride, it is converted into the anhydride, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} > NH$, this being the best way of preparing the last substance. The excess of oxychloride is distilled off under diminished pressure, and the anhydride dissolved in dilute aqueous sodium hydroxide and precipitated with acetic acid.

When *o*-hydrazinobenzoic acid hydrochloride (or, less well, the anhydride) is heated for 4 hours with seven times its weight of phosphorus oxychloride at 120° in a sealed tube, instead of in an open vessel, the product is chloroindazole, $C_6H_4 \begin{smallmatrix} \text{CCl} \\ \text{N} \end{smallmatrix} > NH$ (Bamberger, *Abstr.*, 1899, i, 546), of which the *acetyl* derivative melts at 67° , the *nitroso*-derivative at 89 — 90° . Chloroindazole can be reduced to indazole with zinc powder and strong hydrochloric acid; this must be liberated with ammonia, not with sodium hydroxide, as it forms a compound with zinc hydroxide. It is thus possible to prepare indazole starting from anthranilic acid, which is now a cheap substance. Chloroindazole also forms *methylchloroindazole*, $C_8H_7N_2Cl$, a very feebly basic substance boiling at 268.5° under a pressure of 754 mm., when it is boiled with methyl iodide and methyl alcoholic potassium hydroxide; this yields methylaniline when heated with soda-lime. Further, chloroindazole, when heated at 100° with benzaldehyde in the presence of zinc chloride, forms *benzylidenediindazole*, $CHPh(C_7H_5N_2)_2$, which melts at 140 — 141° , and is insoluble in dilute acids, as well as in water. C. F. B.

Formation of Aromatic Quaternary Ammonium Compounds. By JOHANNES PINNOW (*Ber.*, 1901, 34, 1129—1138. Compare *Abstr.*, 1899, i, 588).—According to Fischer and Windaus (*Abstr.*, 1900, i, 224), a rule similar to Victor Meyer's esterification rule holds for the formation of quaternary ammonium iodides from the tertiary aromatic base and methyl iodide, no quaternary iodide being formed if both the ortho-positions to the dimethylamino-group are replaced. The formation or non-formation of a quaternary ammonium compound is hence suggested as a means of determining the position of the amino-groups in aromatic bases. The authors find, however, that such a rule does not hold in all cases. Thus, neither from *m*-nitrodimethyl-*p*-toluidine nor from nitroacetylaminodimethyltoluidine [$NMe_2 : NHAc : Me : NO_2 = 4 : 3 : 1 : 6$] is an ammonium iodide formed with methyl iodide, whilst

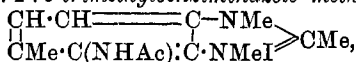
4-acetyl-amino-1:2:5-trimethylbenziminazole (see this vol., i, 139) takes up methyl iodide almost quantitatively.

Pure *m*-nitrodimethyltoluidine and methyl iodide do not combine, but if traces of dinitrotolylmethylnitrosoamine are present, a small quantity of a methiodide is formed.

o-Nitro-*m*-acetylaminodimethyl-*p*-toluidine, $C_{11}H_{15}O_3N_3$, prepared by nitrating the substituted base below 0° , crystallises from a mixture of alcohol and ether in bright yellow, rhombic plates which melt at $142.5\text{--}143^\circ$ (uncorr.), and dissolve readily in chloroform, acetone, or ethyl acetate, less so in alcohol or benzene, and only slightly in ether, light petroleum, or water. This compound only gives a small quantity of methiodide when heated with methyl iodide.

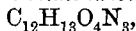
When γ -diacetyldiaminomethyltoluidine is treated with glacial acetic acid, two products are obtained: (1) 4-acetyl-amino-1:2:5-trimethylbenziminazole, which on hydrolysis yields 4-amino-1:2:5-trimethylbenziminazole; the latter yields a tartrate, $C_{10}H_{13}N_3C_4H_6O_6$, crystallising from water in needles arranged in nodular aggregates, and a hydrochloride (+ H_2O) separating in shining, oblique prisms and rhomboidal plates. (2) 7- (or 4-) Acetylmethylamino-2:4- (or 2:7-) dimethylbenziminazole, $\begin{array}{c} \text{CH}\cdot\text{C}(\text{NMeAc})\cdot\text{C}\cdot\text{NH} \\ | \qquad \qquad \qquad | \\ \text{CH}\cdot\text{CMe} \qquad \qquad \text{C}\cdot\text{N} \end{array} \text{ > CMe}$ or $\begin{array}{c} \text{CH}\cdot\text{C}(\text{NMeAc})\cdot\text{C}\cdot\text{N} \\ | \qquad \qquad \qquad | \\ \text{CH}\cdot\text{CMe} \qquad \qquad \text{C}\cdot\text{NH} \end{array} \text{ > CMe}$, which crystallises from water, with $3H_2O$, in slender needles and melts in its water of crystallisation at $64\text{--}65^\circ$, after beginning to sinter at 61° ; when dried by gradual heating to 97° in a vacuum, it melts at $198\text{--}198.5^\circ$ (uncorr.); it is soluble in alcohol, acetone, or ethyl acetate.

4-Acetyl-amino-1:2:5-trimethylbenziminazole methiodide,



prepared from its components either alone or in presence of methyl alcohol, or from γ -diacetyldiaminomethyltoluidine, methyl iodide, and methyl alcohol, separates from a mixture of alcohol and acetone in crystals melting at 232° . When treated with lead acetate and alcohol, the iodine is replaced by an acetyl group, and on oxidising the methyl-acetyl compound thus obtained by means of permanganate, it yields

4-Acetyl-amino-1:3-dimethylbenziminazolone-5-carboxylic acid,



which crystallises from a mixture of alcohol and acetic acid in almost white prisms, remains unmelted at 270° , and is readily soluble in acetic acid.

The following mixtures were experimented with to ascertain if quaternary ammonium compounds could be obtained from them: Dimethyl-*p*-toluidine, methyl alcohol, and hydrobromic acid; *p*-toluidine hydrobromide and methyl alcohol; *p*-toluidine hydrochloride and methyl alcohol; *o*-nitrodimethyl-*p*-toluidine, methyl alcohol, and hydrogen bromide; *p*-toluidine hydrochloride, methyl alcohol, and benzene; dimethyltoluidine, ethyl bromide, and benzene; *o*-nitrodimethyltoluidine, ethyl bromide, and benzene; *o*-acetylaminodimethyl-*p*-toluidine, ethyl bromide, and benzene; *m*-acetylaminodimethyl-*p*-toluidine, methyl iodide, and benzene; *m*-acetylaminodimethyl-*p*-toluidine, ethyl bromide, and benzene.

ene. The results are arranged in tabular form. The following quaternary salts were isolated.

o-Nitro-*p*-tolyltrimethylammonium bromide, $C_{10}H_{14}O_2N_2 \cdot HBr$, crystallises from alcohol in clusters of bright yellow, oblique prisms which melt at 182° (uncorr.) and dissolve readily in water.

o-Acetyl-amino-*p*-tolyl-dimethylethylammonium bromide, $C_{13}H_{20}ON_2 \cdot HBr$, melts at 187.5° (uncorr.), but could not be obtained crystalline as it is too soluble in water, alcohol, or aqueous acetone and not sufficiently so in other solvents.

m-Acetyl-amino-*p*-tolyltrimethylammonium iodide, $C_{12}H_{18}ON_2 \cdot HI$, crystallises from a mixture of alcohol and ether in rhombic needles having a brilliant lustre and melting at 193.5° (uncorr.); it is soluble in alcohol or water but insoluble in ether.

The presence of water hinders the formation of the quaternary ammonium salts.
T. H. P.

Quinoxaline Group. I. By C. MANUELLI and M. GALLONI (*Gazzetta*, 1901, 31, i, 18—26).—The action of anhydrous oxalic acid on diacetyl-*o*-phenylenediamine gives rise to three products: (1) methylbenziminazole; (2) monoacetyl-*o*-phenylenediamine, $C_8H_9ON_2$, which melts at 145° and is soluble in water, alcohol, or ether; (3) monoacetyldioxyquinoxaline, $C_6H_4 \begin{smallmatrix} \text{N} \text{---} \text{Ac} \cdot \text{CO} \\ \text{N} \text{---} \text{C} \cdot \text{OH} \end{smallmatrix}$ or $C_6H_4 \begin{smallmatrix} \text{N} \text{---} \text{Ac} \cdot \text{CO} \\ \text{NH} \text{---} \text{CO} \end{smallmatrix}$, which crystallises from water in small, white prisms melting at 184° ; it dissolves in alcohol, chloroform, acetic acid, or aqueous alkali hydroxides, and to a slight extent in benzene or ether. The hydrochloride, $C_{10}H_8O_3N_2 \cdot HCl$, is very soluble in water or alcohol and melts at 176.5° ; the platinichloride, $(C_{10}H_8O_3N_2)_2 \cdot H_2PtCl_6$, separates from ether in shining, yellow prisms melting at 215° ; the mercurichloride, $(C_{10}H_8O_3N_2)_2 \cdot HgCl_2$, crystallises from dilute hydrochloric acid in long, white prisms melting at 191 — 192° ; the diethiodide, $C_{10}H_8O_3N_2 \cdot 2EtI$, separates from alcohol in long, slender, dark red, unstable needles melting at 115° . No oxime or phenylhydrazone could be prepared.
T. H. P.

Iminazoles of the Benzene and Naphthalene Series. By OTTO FISCHER (*Ber.*, 1901, 34, 930—940. Compare *Abstr.*, 1899, i, 641).—[With O. FEZER and LUDWIG REINDL.]—1-Ethyl-*a*-naphthiminazole, $CH \begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{NEt} \\ \text{CH} \text{---} \text{C} \text{---} \text{N} \end{smallmatrix} CH$, prepared by heating, at 110° , naphthiminazole (m. p. 174°) with ethyl iodide and absolute alcohol, crystallises from ether in colourless prisms and melts at 129 — 130° ; its hydriodide is not completely decomposed by cold aqueous sodium hydroxide solution, the base being, however, set free by digesting the salt with alcoholic potassium hydroxide. The platinichloride crystallises in pale yellow needles, and the mercurichloride in colourless needles, the latter melting at 162° .

1-Methyl-*a*-naphthiminazole crystallises from ether or alcohol in colourless needles melting at 88° . The platinichloride and aurichloride separate from alcohol in yellow needles.

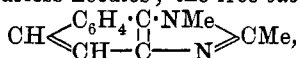
1-Acetyl-*a*-naphthiminazole, produced by treating naphthiminazole with acetic chloride in pyridine solution, crystallises from benzene in

white needles and melts at 153° ; the corresponding *benzoyl* derivative, obtained by the Schotten-Baumann reaction, melts at 120° .

3-Ethyl- β -naphthiminazole, $\text{CH} \begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \\ \text{CH} - \text{C} \cdot \text{NEt} \end{smallmatrix} \text{CH}$, obtained by heating β -ethyl-1:2-naphthylenediamine with formic acid, is an oil distillable under reduced pressure; the *hydrochloride* crystallises from alcohol in colourless needles and melts at 226° ; the *mercurichloride* forms slightly soluble, white needles and melts at 182° .

2-Methyl- α -naphthiminazole, $\text{CH} \begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{NH} \\ \text{CH} - \text{C} \cdot \text{N} \end{smallmatrix} \text{CMe}$, prepared by heating at 140° for 12 hours a mixture of 1:2-naphthylenediamine hydrochloride, sodium acetate, and glacial acetic acid, is obtained in the form of its *hydrochloride* by extracting the product of reaction with water and allowing the solution to crystallise; the free base is slightly soluble in water or ether and crystallises from methyl alcohol in lustrous prisms melting at 168 – 169° . The *mercurichloride* crystallises in white prisms, and the *aureichloride*, $\text{C}_{12}\text{H}_{11}\text{N}_2\text{Cl}_4\text{Au}$, in orange needles; the *platinichloride*, when separating from hot aqueous solutions, contains $3\text{H}_2\text{O}$, this water being eliminated at 110 – 120° .

1:2-Dimethyl- α -naphthiminazole *hydriodide*, prepared by heating the preceding base with methyl iodide at 100° , crystallises from hot water in aggregates of colourless needles; the free base,



crystallises from dilute alcohol in colourless needles and melts at 143 – 144° ; the *platini-* and *aureichlorides* crystallise in yellow needles.

2-Phenyl- α -naphthiminazole, produced on heating at 160° a mixture of 1:2-naphthylenediamine hydrochloride, sodium benzoate, and benzoic acid, is isolated in the form of its *benzoate*, this salt separating from alcoholic solutions in white, nodular crystals; the base separates from dilute alcohol in colourless crystals melting at 217° . The *nitrate* and *sulphate* crystallise in white needles, the *aureichloride* in reddish-brown prisms melting at 207° , and the *platinichloride* in pale yellow needles with $2\text{H}_2\text{O}$.

[With E. FUSSENEGGER.]—1:3-Dimethylbenziminazole *iodide*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NMe} \\ \text{NMeI} \end{smallmatrix} \text{CH}$, obtained by heating benziminazole with methyl iodide and methyl alcohol at 140 – 150° , melts at 144° .

1:3-Dimethylbenziminazolone, prepared either by treating the preceding compound with sodium hydroxide or by the action of formic acid on *s*-dimethyl-*o*-phenylenediamine, crystallises in white needles and melts at 74 – 75° ; its *hydrochloride* melts at 247° ; the second method of preparation indicates that the base has the constitution of a carbinol, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NMe} \\ \text{NMe} \end{smallmatrix} \text{CH} \cdot \text{OH}$ (compare Pinnow and Sämann, Abstr., 1899, i, 943). The *platinichloride* and *aureichloride* do not contain oxygen; the former crystallises in red prisms, the latter in yellow needles.

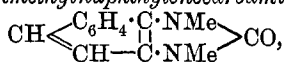
s-Dimethyl-*o*-phenylenediamine, $\text{C}_6\text{H}_4(\text{NHMe})_2$, produced by hydrolysing the preceding base or its salts with aqueous sodium hydroxide solution, is distillable in steam, boils at 245 – 255° , and melts at

34—35°; it forms crystallisable salts, the *hydrochloride* melting at 180°. A solution of the hydrochloride develops, with ferric chloride a red coloration, and a hydrochloride, crystallising in green leaflets, is subsequently produced; this product, which readily dissolves in water, is less soluble in alcohol and yields a yellow base.

s-Dimethyl-*o*-phenylenediamine, when condensed with acetic anhydride, yields 1:2:3-trimethylbenziminazolone (compare Pinnow and Sämann, *loc. cit.*), this synthesis confirming the constitution ascribed to the substance.

Dimethylphenylenecarbamide, $C_6H_4 \begin{smallmatrix} \diagup NMe \\ \diagdown NMe \end{smallmatrix} CO$, is readily obtained from 1:3-dimethylbenziminazolone either by oxidation with potassium permanganate or by dry distillation; in the latter process, 1-methylbenziminazole is simultaneously produced.

1:3-Dimethylnaphthiminazolone, $CH \begin{smallmatrix} \diagup C_6H_4 \cdot C \cdot NMe \\ \diagdown CH - C \cdot NMe \end{smallmatrix} CH \cdot OH$, produced by the action of methyl iodide and methyl alcohol on 1-methyl-*a*-naphthiminazole or naphthiminazole, crystallises in colourless prisms and melts at 123°; when boiled with aqueous sodium hydroxide solution, oxidised with potassium permanganate, or subjected to dry distillation, it yields *dimethylnaphthylenecarbamide*,



this compound crystallising from alcohol in white prisms and melting at 171°.
G. T. M.

Isatin and its Derivatives. VI. By LEO MARCHLEWSKI and J. SOSNOWSKI (*Ber.*, 1901, **34**, 1108—1112).—The compound formed by the hydrolysis of the product of condensing acetylisatin with *o*-phenylenediamine is not *o*-aminophenimesatin (*Abstr.*, 1896, i, 235) but

2-hydroxy-3-*o*-aminophenylquinoxaline, $NH_2 \cdot C_6H_4 \cdot C \cdot N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} OH \\ C \cdot N \end{smallmatrix} > C_6H_4$; when hydrochloric acid and sodium nitrite are added to its boiling alcoholic solution, it yields *cumarophenazine*, $C_6H_4 \cdot C \cdot N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} O \\ C \cdot N \end{smallmatrix} > C_6H_4$, which crys-

tallises from dilute alcohol in lustrous, scaly aggregates of slender needles or in long, yellow needles, melts at 168° (uncorr.), and sublimes unchanged at higher temperatures. Although a neutral substance, it dissolves in boiling alkalis to form 2-hydroxy-3-*o*-hydroxyphenylquinoxaline, $OH \cdot C_6H_4 \cdot C \cdot N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} OH \\ C \cdot N \end{smallmatrix} > C_6H_4$, which crystallises from alcohol in dark yellow

needles, melts at 296° (uncorr.) (289° when slowly heated), and readily yields a *monosulphonic acid* crystallising in slender, golden needles; the *sodium* salt of the latter crystallises from a mixture of water and alcohol in long, yellowish-brown needles containing water of crystallisation, and the *barium* salt forms bright yellow needles and is sparingly soluble in water.

Methylcumarophenazine, $C_6H_4 \cdot C \cdot N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} O \\ C \cdot N \end{smallmatrix} > C_6H_3Me$, obtained by the action

of hydrochloric acid and sodium nitrite on 2-hydroxy-3-o-aminophenyl-6-(or 7)-methylquinoxaline, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \begin{smallmatrix} \text{OH} \\ \text{C} \cdot \text{N} \end{smallmatrix} > \text{C}_6\text{H}_3\text{Me}$ (to be described later), separates from alcohol in white crystals, melts at $133-134^\circ$ (uncorr.), and closely resembles its homologue; thus, when boiled with alkalis, it yields 2-hydroxy-3-o-hydroxyphenyl-6-(or 7)-methylquinoxaline, which melts at 161° and is easily sulphonated.

Both cumarophenazine and methylcumarophenazine show a blue fluorescence in alcoholic solution. W. A. D.

Isatin. VII. By LEO MARCHLEWSKI and L. G. RADCLIFFE (*Ber.*, 1901, **34**, 1113—1115).—Isatin interacts with ethyl-o-tolylenediamine, $\text{NHEt} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$ [$\text{Me} : \text{NH}_2 : \text{NHEt} = 1 : 3 : 4$], in glacial acetic acid, not as a diketone, but as a hydroxyketone, to form 5-ethyl-2 methyl- ψ -indophenazine, $\begin{smallmatrix} \text{CH} : \text{CH} : \text{C} \\ \text{CH} : \text{CH} : \text{C} \end{smallmatrix} \begin{smallmatrix} \text{C} \\ \text{C} \end{smallmatrix} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{C} \\ \text{C} \end{smallmatrix} \begin{smallmatrix} \text{CH} : \text{CMe} \\ \text{CH} : \text{CH} \end{smallmatrix}$; this crystallises from dilute alcohol in lustrous red needles, melts at 213° , and yields yellow salts which are hydrolysed by hot water.

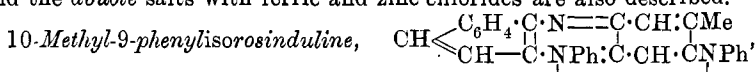
It is probable that isatin does not react initially as a hydroxyketone, but that the compound $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} > \text{C} : \text{N} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NHEt}$ is first formed which successively yields $\text{N} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}(\text{OH}) \end{smallmatrix} > \text{C} : \text{N} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NHEt}$ and $\begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{C} = \text{N} \\ \text{N} = \text{C} \cdot \text{NEt} \end{smallmatrix} > \text{C}_6\text{H}_3\text{Me}$. W. A. D.

Study of the isoRosinduline and isoRosindone Reactions. By OTTO FISCHER (*Ber.*, 1901, **34**, 940—949).—[with G. A. BRUHN].

10-Methylisorosindonehydrochloride, $\text{CH} \begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \\ \text{CH} - \text{C} \cdot \text{NPhCl} \end{smallmatrix} \begin{smallmatrix} \text{C} \cdot \text{CH} : \text{CMe} \\ \text{C} \cdot \text{CH} : \text{C} \cdot \text{OH} \end{smallmatrix}$, prepared by mixing together nitroso-o-cresol and phenyl- β -naphthylamine in alcoholic hydrochloric acid solution and gently heating the mixture, is precipitated on the addition of water in the form of red, silky needles; the base crystallises from 70 per cent. alcohol in reddish-brown needles having a metallic lustre and melting at 258° ; it dissolves in the ordinary organic solvents, but is insoluble in water. The compound is only slightly basic; its salts, although readily crystallisable, being dissociated by water or alcohol. The hydriodide and hydrobromide crystallise in felted red needles, the nitrate and sulphate in yellow needles. The aurichloride crystallises in red prisms and has an abnormal composition, $(\text{C}_{28}\text{H}_{16}\text{N}_2\text{O})_2 \cdot \text{HAuCl}_4$; the platinichloride, $(\text{C}_{28}\text{H}_{16}\text{N}_2\text{O})_2 \cdot \text{H}_2\text{PtCl}_6$, forms aggregates of orange-red needles; the mercurichloride separates in prisms, the ferrichloride crystallises in green leaflets which appear red by transmitted light.

10-Methylchlorophenyl-naphthaphenazonium chloride, $\text{C}_{28}\text{H}_{16}\text{N}_2\text{Cl}_2$, results from the action of phosphorus pentachloride and phosphorus oxychloride on the 10-methylisorosindone and crystallises from alcohol or ether in reddish-yellow needles; it is readily soluble in water or alcohol, crystallising from the former solvent on the addition of sodium chloride in brownish-red needles. One of the chlorine atoms contained in this compound is readily exchanged for the bromine, iodine, or NO_2 .

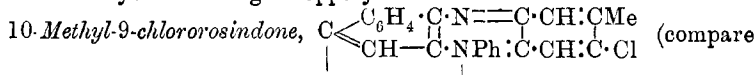
ion, by double decomposition in aqueous or alcoholic solution; the *bromide*, $C_{23}H_{16}N_2ClBr$, obtained by the interaction of potassium bromide, separates in leaflets or brownish-red, acicular crystals, the *iodide* and *nitrate* crystallising in lustrous, green leaflets. The *platini-* and *auro-chlorides* crystallise in orange needles; the *mercurichlorides* and the *double salts* with ferric and zinc chlorides are also described.



obtained in the form of its *hydrochloride* by heating an alcoholic solution of 10-methylchlorophenyl-naphthaphenazonium chloride and aniline (2 mols.), separates from benzene in crystals having a bronzy reflex; the *hydrobromide*, *hydriodide*, and *nitrate* are crystalline, yellow salts.

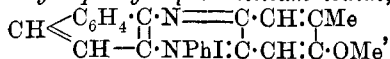
10-Methyl-9-tolylisorosinduline, similarly prepared by substituting *p*-toluidine for aniline in the preceding reaction, separates from dilute alcohol in dark blue crystals and melts at $225^\circ - 226^\circ$.

10-Methyl-9- β -naphthylisorosinduline crystallises from benzene in light blue prisms having a grey metallic lustre; its *hydrochloride* crystallises in lustrous, black leaflets, and the *nitrate* separates from alcohol in crystals having a coppery reflex.



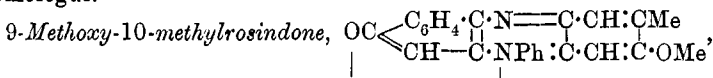
Abstr., 1900, i, 460), produced by boiling 10-methylchlorophenyl-naphthaphenazonium chloride with an aqueous solution of sodium acetate, crystallises from alcohol in orange leaflets with a bronzy reflex, it is soluble in the ordinary organic solvents and sublimes at 300° with partial decomposition; its solution in concentrated sulphuric acid is dichroic, being blue by reflected, and red by transmitted light.

9-Methoxy-10-methyl-7-phenyl-naphthazonium iodide,



formed by heating 10-methylisorosindone with excess of methyl iodide at 100° , crystallises from alcohol in lustrous, green needles; on treatment with nitric acid, it yields the *nitrate* which also separates in green needles.

9-Ethoxy-10-methyl-7-phenyl-naphthazonium iodide resembles its lower homologue.



produced by heating the preceding methoxy-iodide with alcoholic potassium hydroxide, crystallises from alcohol in brownish-red needles melting at $287 - 288^\circ$; its solution in concentrated sulphuric acid is dichroic. These results indicate that the indone produced from nitroso-*o*-cresol is in all respects analogous with *isorosindone*.

[With M. VON CAMMERLOHER.]—The isomeric *methylisorosindone* obtained in the form of its *hydrochloride* by the interaction of nitroso-*m*-cresol and phenyl- β -naphthylamine in alcoholic hydrochloric acid solution, crystallises from dilute alcohol in needles having a bronze

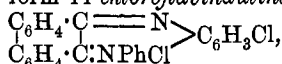
reflex; the base is soluble in the ordinary organic solvents but not in water, its salts are dissociated by the latter medium. The *hydriodide* crystallises in green needles, the *hydrobromide* in yellow needles, and the *nitrate* in prisms having a bronze reflex. The *platinichloride* and *mercurichloride* crystallise in red needles.

2-Nitroso-1:3:5 *xyleneol* crystallises from alcohol in yellow prisms and melts at 175°; it is insoluble in water but dissolves in the ordinary organic solvents and ammonia solution.

6-Nitroso-1:2:3-*xyleneol* crystallises in yellow needles and melts at 166°.

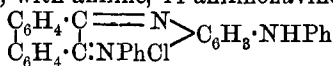
2-Nitroso-1:3:5-*ethylxylylidine*, prepared by ethylating *s*-xylylidine with ethyl bromide, treating the product with nitrous acid, heating the nitrosoamine with alcoholic hydrochloric acid, and decomposing the yellow *hydrochloride* produced with ammonia, crystallises from benzene in steel-blue prisms and melts at 138°. G. T. M.

Chloro-derivatives of Azonium Dyes. I. By FRIEDRICH KEHRMANN and WALTHER HIBY (*Ber.*, 1901, 34, 1085—1095).—5-Chloro-2-aminodiphenylamine *hydrochloride*, prepared from Laubheimer's 5-chloro-2-nitrodiphenylamine (*Abstr.*, 1876, ii, 294), condenses at the ordinary temperature with phenanthraquinone in glacial acetic acid solution to form 11-chloroflavinduline chloride,

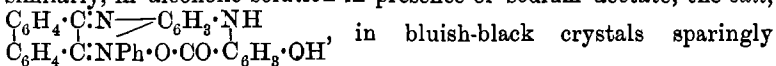


which separates from alcohol in large crystals of the colour of potassium dichromate; the corresponding *nitrate* crystallises from alcohol in blood-red prisms with a greenish lustre. The *base*, $\text{C}_{26}\text{H}_{16}\text{N}_2\text{Cl} \cdot \text{OH}$, is a yellowish-green powder which cannot be recrystallised owing to decomposition occurring; when heated with acetic anhydride, it yields, not the acetyl derivative of the pseudo-form, but the acetate of the azonium base.

Aromatic bases interact with 11-chloroflavinduline chloride to form compounds identical with those obtained by their direct action on flavinduline. Thus, with aniline, 11-anilinoflavinduline chloride,



(German Patent, 97639), is obtained. *p*-Aminosalicylic acid yields similarly, in alcoholic solution in presence of sodium acetate, the salt,

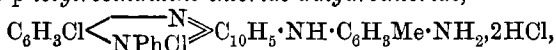


in bluish-black crystals sparingly soluble in all solvents, but dissolving in hot alcoholic hydrochloric acid to form the *chloride*, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \equiv \text{N} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{NPhCl} \end{array} > \text{C}_6\text{H}_3 \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO}_2\text{H}$, which separates in violet needles.

10-Chloro-12-phenylisonaphthaphenazonium 12-nitrate, prepared by condensing 5-chloro-2-aminodiphenylamine sulphate with β -naphthaquinone and salting out with solid sodium nitrate, crystallises from alcohol in brownish-red granules; with aqueous-alcoholic dimethylamine, it yields 10-dimethylamino-12 phenylisonaphthaphenazonium 12 nitrate (*Abstr.*, 1898, i, 154), whilst with *p*-aminosalicylic acid it

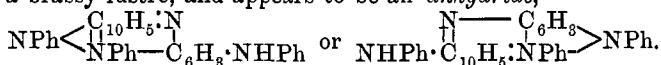
forms an internal salt, $C_{20}H_{10}O_3N_3$, crystallising in greenish needles and analogous to that obtained similarly from 11-chloroflavinduline.

10-Chlorophenylrosinduline chloride (10-chloro-5-anilino-7-phenylphenazonium 7-chloride), prepared from 5-chloro-2-aminodiphenylamine hydrochloride and 4-anilino- β -naphthaquinone, crystallises from absolute alcohol in dark green prisms; 10-chloro-5-*p*-tolylrosinduline chloride, obtained similarly, using 4-toluidino- β -naphthaquinone, crystallises from alcohol in slender needles with a bronzy lustre, whilst 10-chloro- β -naphthylrosinduline chloride is a reddish-brown, crystalline powder only sparingly soluble in water and alcohol. 10-Chloro-6-*m*-amino-*p*-tolylrosinduline chloride dihydrochloride,



obtained by using *m*-tolylenediamino- β -naphthaquinone, separates from alcohol in crystals with a green, metallic lustre.

When the 10-chlororosindulines are boiled with aromatic bases, the halogen atom is replaced by an amino-radicle, naphthaphenosafraanine derivatives being formed. Diphenylnaphthaphenosafraanine chloride (5:9-dianilino-7-phenylnaphthaphenazonium 7-chloride), obtained by using aniline, crystallises from alcohol in granules with a coppery lustre; the derived base crystallises from water in greenish needles with a brassy lustre, and appears to be an anhydride,



Di-*p*-tolylnaphthaphenosafraanine chloride, prepared from chloro-*p*-tolylrosinduline chloride and *p*-toluidine, separates from boiling alcohol in bronze-coloured crystals, and yields a base which forms green crystals from a mixture of benzene and alcohol, and is an anhydride like its lower homologue.

W. A. D.

Chloro-derivatives of Azonium Dyes. II. By FRIEDRICH KEHRMANN and H. MÜLLER (*Ber.*, 1901, **34**, 1095—1101).—3-Chloro-6-nitromethylaniline, prepared by the interaction of 1-chloro-3:4-dinitrobenzene and aqueous methylamine in alcoholic solution at the ordinary temperature, crystallises from alcohol in orange-red needles, melts at 104—105°, and on reduction yields 4-chloro-*o*-phenylenemethyldiamine. The hydrochloride of this condenses with 4-amino-1:2-naphthaquinone in boiling alcoholic solution to form 9-chloro-5-amino-7-methylnaphthaphenazonium 7-chloride, which crystallises from alcohol in small, ruby-red prisms with a golden sheen, and shows an intense red fluorescence in alcoholic solution; the nitrate forms slender, crimson needles, and the platinichloride and dichromate garnet-coloured, crystalline powders. With 4-anilino-1:2-naphthaquinone, 9-chloro-5-anilino-7-methylnaphthaphenazonium chloride is obtained; it crystallises from alcohol in sheaf-like aggregates of dark-red needles; the dichromate and platinichloride are dark-red, crystalline powders.

9-Chloro-5-sulphanilino-7-methylnaphthaphenazonium-3-sulphonic acid, $N \equiv C_{10}H_4(SO_3H)NH$, $C_6H_5Cl \cdot NMe \cdot O \cdot SO_2 \cdot C_6H_4$, H_2O , prepared by combining 3-chloro-6-aminomethylaniline hydrochloride with sodium-4-sulphanilino-1:2-

naphthaquinone-6-sulphonate (made from sodium sulphanilate and potassium 4:6- β -naphthaquinonedisulphonate) in aqueous solution at 100°, and precipitating with hydrochloric acid, forms small, glittering red crystals with a golden lustre.

9-Chloro-5-*p*-acetylaminoanilino-7-methylnaphthaphenazonium-3-sulphonic acid, $\text{N} \equiv \text{C}_{10}\text{H}_4(\text{SO}_2) \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, $\text{C}_6\text{H}_3\text{Cl} \cdot \text{NMe} \cdot \text{O}$, H_2O , obtained similarly from the quinoneanilide prepared from *p*-aminoacetanilide and potassium β -naphthaquinone-4:6-disulphonate, separates from glacial acetic acid in violet-brown crystals; from the mother liquors, on long standing, 10-chloro-5-hydroxy-12-methylisonaphthaphenazonium-3-sulphonic acid, $\text{N} \equiv \text{C}_{10}\text{H}_4(\text{OH}) \cdot \text{SO}_2$, $\text{C}_6\text{H}_3\text{Cl} \cdot \text{NMe} \cdot \text{O}$, separates as a brownish-red, crystalline powder.

9-Chloro-7-methylrosindone, $\text{N} \equiv \text{C}_{10}\text{H}_4 \cdot \text{O}$, $\text{C}_6\text{H}_3\text{Cl} \cdot \text{NMe}$, prepared by leaving 4-hydroxy- β -naphthaquinone and 3-chloro-6-aminomethylaniline in alcoholic solution at the ordinary temperature, crystallises from benzene in garnet-coloured leaflets with a golden lustre; simultaneously there is formed the isomeric 10-chloro-12-methylprasindone, which is insoluble in benzene and yields a chloride crystallising in lustrous black needles. W. A. D.

Chloro-derivatives of Azonium Dyes. III. By FRIEDRICH KEHRMANN and S. KRAZLER (*Ber.*, 1901, **34**, 1102—1108).—3-Chloro-6-nitrophenyl-*p*-tolylamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, prepared by heating 1-chloro-3:4-dinitrobenzene with *p*-toluidine and anhydrous sodium acetate at 100°, crystallises from light petroleum in scarlet needles and melts at 126°; 3-chloro-6-nitro-4'-acetylamino-diphenylamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, obtained similarly, using *p*-amino-acetylanilide, crystallises from alcohol in lustrous, red needles and melts at 221°. On reduction with stannous chloride and alcoholic hydrochloric acid, the foregoing nitro-compounds yield respectively 3-chloro-6-aminophenyl-*p*-tolylamine, and 3-chloro-6:4'-diaminodiphenylamine.

9-Chlororosinduline chloride (9-chloro-5-amino-7-phenylnaphthaphenazonium 7-chloride), prepared by boiling together 4-amino-1:2-naphthaquinone and 3-chloro-6-aminodiphenylamine in alcoholic solution, separates from alcohol, to which it imparts a red fluorescence, in garnet-red crystals; the dichromate is a blood-red, crystalline powder.

9-Chloro-5-*p*-toluidino-7-*p*-tolyl-naphthaphenazonium 7-chloride, prepared by boiling 4-*p*-toluidino-1:2-naphthaquinone with 3-chloro-6-aminophenyl-*p*-tolylamine in alcoholic solution, crystallises in aggregates of four-sided prisms with a greenish, metallic lustre; the derived base forms brassy needles, and is the anhydride $\text{C}_{30}\text{H}_{22}\text{N}_3\text{Cl}$. On boiling the chloride with *p*-toluidine, the safranine dye, 5:9-di-*p*-toluidino-7-*p*-tolyl-naphthaphenazonium chloride, is obtained in blue crystals with a golden lustre.

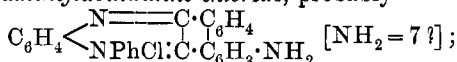
9-Chloro-5-amino-7-*p*-aminophenylnaphthaphenazonium chloride, prepared from the foregoing 3-chloro-6:4'-diaminodiphenylamine and

4-amino-1:2-naphthaquinone, crystallises from alcohol, to which it imparts a brownish-red fluorescence, in dark brown crystals with a bronzy lustre; the *dichromate* is a dark brown, crystalline powder. Acetic anhydride at the ordinary temperature acetylates only the amino-group in the 7-phenyl nucleus of the foregoing chloride, the red *acetyl* derivative obtained crystallising from alcohol; on eliminating the unattacked amino-group by the diazo-reaction, and hydrolysing the acetyl derivative so formed, a new *chloroisorosinduline* (9-chloro-7-p-aminophenyl-naphthaphenazonium) is obtained; the *bromide* crystallises from water either in slender, orange-yellow plates, or, when grown more slowly, in thick prisms with a dark green, metallic lustre, and the *dichromate* is a dark brown, crystalline powder. W. A. D.

Nitro- and Amino-flavindulines. By FRIEDRICH KEHRMANN and JOSEF EICHLER (*Ber.*, 1901, **34**, 1210—1217).—11-Piperidino-flavinduline, $\text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \text{---} \text{C} \cdot \text{CH} \cdot \text{CH}$
 $\text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{NPhCl} \cdot \text{C} \cdot \text{CH} \cdot \text{C}_5\text{NH}_{10}$, prepared by the action of piperidine on a cold alcoholic solution of flavinduline chloride, forms dark blue needles with a copper-like lustre; the *dichromate*, $(\text{C}_{31}\text{H}_{26}\text{N}_3)_2\text{Cr}_2\text{O}_7$, is a blue-green, crystalline precipitate.

Phenanthrarosinduline, $\text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \text{---} \text{C} \cdot \text{C}_6\text{H}_4 \gg \text{C} \cdot \text{NH}_2$, prepared by the action of ammonia and air on naphthaflavinduline chloride, crystallises from alcohol in dark red prisms with a bronze-like lustre; the *dichromate*, $(\text{C}_{30}\text{H}_{20}\text{N}_3)_2\text{Cr}_2\text{O}_7$, forms a dark red, crystalline precipitate. *Phenylphenanthrarosinduline*, $\text{C}_{36}\text{H}_{24}\text{N}_3\text{Cl}$, prepared by the action of aniline on naphthaflavinduline, forms large, dark violet crystals with a copper-like lustre.

When treated with cold concentrated nitric acid, flavinduline nitrate gives a mixture of nitro-derivatives, of which only one was isolated; this *nitroflavinduline nitrate*, $\text{C}_{26}\text{H}_{16}\text{N}_3\text{O}_4$, crystallises from alcohol in glistening, straw-yellow needles, and is reduced by stannous chloride to an *aminoflavinduline chloride*, probably



the *dichromate* is an olive-green, crystalline precipitate; the *platini-chloride* resembles the dichromate; the aminoflavinduline closely resembles Kehrman and Kikine's diaminoflavinduline (*Abstr.*, 1900, i, 61) and isorosinduline No. 12 (this vol., i, 101). A second aminoflavinduline is formed on reducing the mother liquors of the nitroflavinduline, which is identical with that previously described (*Abstr.*, 1900, i, 61), and probably contains the amino-group in the 3-position.

T. M. L.

Fluorindine. By FRIEDRICH KEHRMANN and BERNHARD GUGGENHEIM (*Ber.*, 1901, **34**, 1217—1224).—*Chloroanilinoaposafranine chloride*, $\text{C}_6\text{H}_5\text{Cl} \begin{array}{l} \text{N} \text{---} \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{NHPh} \\ \text{NPhCl} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{NH}_2 \end{array}$, is produced by oxidation of chloroaminodiphenylamine with ferric chloride; it was prepared by Ernst (*Abstr.*, 1891, 299), but not analysed; it crystallises from

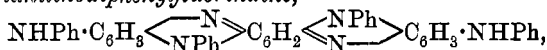
alcohol in greenish needles with a metallic lustre, whilst the base separates in black, glistening tablets.

Dichlorodiphenylfluorindine, $\text{C}_6\text{H}_5\text{Cl} \begin{smallmatrix} \text{N} \\ \text{NPh} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{NPh} \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_5\text{Cl}$, prepared by heating the preceding compound with Laubenheimer's diamine and benzoic acid, crystallises in violet-grey needles; the *hydrochloride* crystallises in needles with a brass-like lustre, and the *dihydrochloride* in copper coloured scales.

Chlorodiphenylfluorindine, $\text{C}_6\text{H}_5\text{Cl} \begin{smallmatrix} \text{N} \\ \text{NPh} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{NPh} \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_4$, prepared by condensing the aposafranine chloride with *o*-aminodiphenylamine, crystallises from nitrobenzene or ethyl benzoate, forms red-violet needles with a metallic lustre, and melts above 360° ; it forms a copper-red *dihydrochloride*, and a brass-like *monohydrochloride*.

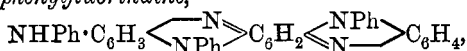
Chlorophenylfluorindine, $\text{C}_6\text{H}_5\text{Cl} \begin{smallmatrix} \text{N} \\ \text{NPh} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_4$, prepared by condensing the aposafranine chloride with *o*-phenylenediamine, is a dark red, crystalline powder; the *monohydrochloride* crystallises from alcohol in green needles with a metallic lustre; the base does not appear to give a dihydrochloride.

3 : 10-*Dianilinodiphenylfluorindine*,



prepared by heating dichlorodiphenylfluorindine hydrochloride with aniline and aniline hydrochloride crystallises from a mixture of alcohol and benzene; the *hydrochloride*, $\text{C}_{42}\text{H}_{30}\text{N}_6 \cdot \text{HCl}$, crystallises from alcohol in flakes with a bronze-like lustre.

3-*Anilinodiphenylfluorindine*,



prepared by the action of aniline and aniline hydrochloride on chlorodiphenylfluorindine hydrochloride, crystallises from a mixture of alcohol and benzene in dark blue flakes with a green lustre; the *hydrochloride* crystallises from alcohol, in which it is less soluble than the hydrochloride of the dianilino-base.

Nitrodiphenylfluorindine, $\text{C}_{30}\text{H}_{19}\text{N}_4 \cdot \text{NO}_2$, prepared by adding the theoretical quantity of potassium nitrate to a solution of diphenylfluorindine in sulphuric acid, is a greenish-grey, crystalline powder soluble in boiling nitrobenzene.

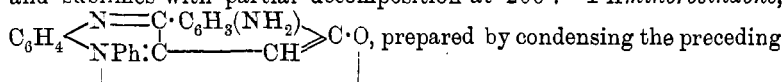
Nitrophenylfluorindine, $\text{C}_{24}\text{H}_{15}\text{N}_4 \cdot \text{NO}_2$, prepared in a similar manner from phenylfluorindine, forms minute, brown-red scales with a golden lustre.

T. M. L.

Constitution of *iso*Rosinduline No. 8. Derivatives of Trinitro- α -naphthol $[\text{OH} : (\text{NO}_2)_3 = 1 : 2 : 4 : 8]$. By FRIEDRICH KEHRMANN and EMILE MISSLIN (*Ber.*, 1901, **34**, 1224—1233).—By reducing 2 : 4 : 8 trinitro-1-naphthol, and then oxidising by means of a current of air,

2 : 8-diamino-1 : 4-naphthaquinoneimine, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} & \text{C} \cdot \text{NH}_2 \\ | & | \\ \text{C}(\text{NH}) & \text{CH} \end{smallmatrix}$, is produced; the *hydrochloride* forms red-brown needles with a metallic

lustre. By heating with ammonia, the quinoneimine is converted into diamino- α - and β -naphthaquinones, whilst sodium hydroxide gives 8-amino-2-hydroxy-1:4-naphthaquinone, which crystallises from alcohol in dark brown needles with a green, metallic lustre, and begins to sublime with partial decomposition at 225° ; the acetyl derivative of the quinone crystallises from water in dark brown, glistening needles, and sublimes with partial decomposition at 200° . 1-Aminorosindone,

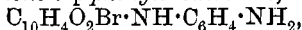


acetyl derivative with phenyl-*o*-phenylenediamine, crystallises from alcohol in dark red needles with a brass-like lustre, and gives an acetyl derivative which crystallises in red-brown flakes and sublimes at 300° ; this acetyl derivative can also be prepared from isorosinduline No. 8 (Abstr., 1900, i, 60) by acetylation and subsequent oxidation, and the latter is thus shown to be a 1-aminophenylnaphthaphenazonium salt.

The two diamionaphthaquinones obtained by the action of ammonia on 2:8-diamino-1:4-naphthaquinoneimine can be separated by reducing to the quinols, converting into tetracetates, and then by hydrolysis and oxidation into diacetylaminquinones. 4:8-Diacetylamino-1:2-naphthaquinone is soluble in alcohol, crystallises from acetic acid in glistening, brownish-yellow flakes, and melts at 225° .

4:8-Diacetylamino-1:4-naphthaquinone is insoluble in alcohol, but crystallises from acetic acid in glistening, red flakes, and melts and decomposes at $240\text{--}245^\circ$. It condenses with *o*-phenylenediamine to 1:5-diacetylaminonaphthaphenazine, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \text{N} \end{array} \text{C}_{10}\text{H}_4(\text{NHAc})_2$, which crystallises from nitrobenzene in minute, golden-yellow needles; 1:5-diaminonaphthaphenazine, $\text{C}_{16}\text{H}_{12}\text{N}_4$, crystallises from nitrobenzene in yellowish-red needles with a brass-like lustre. T. M. L.

Action of 2:3-Dibromo- α -naphthaquinone on *o*-, *m*-, and *p*-Phenylenediamine and some new Derivatives of $\alpha\beta$ -Naphthaphenazine. By S. LINDENBAUM (Ber., 1901, 34, 1050—1060).—2-Bromo- α -naphthaquinone-3-*p*-phenylenediamine,



obtained by the action of dibromonaphthaquinone on an alcoholic solution of *p*-phenylenediamine and sodium ethoxide, crystallises from alcohol in deep blue, lustrous plates, is sparingly soluble in ether, light petroleum, or benzene, but more readily in hot alcohol or glacial acetic acid, and does not melt below 350° ; it dissolves in sulphuric acid with formation of bromohydroxynaphthaquinone.

2-Bromo- α -naphthaquinone-3-*m*-phenylenediamine crystallises from alcohol in copper-coloured, lustrous plates and melts at $194\text{--}195^\circ$; its solubilities and behaviour with sulphuric acid resemble those of the *p*-compound.

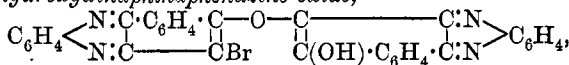
6-Bromo-5-hydroxy- $\alpha\beta$ -naphthaphenazine (6-bromo- α -naphtheurhodole), $\text{OH} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \begin{array}{c} \text{N} \\ \text{CBr} \text{---} \text{C} \cdot \text{N} \end{array} \text{C}_6\text{H}_4$, is obtained by the action of dibromonaphthaquinone on *o*-phenylenediamine in presence of potassium ethoxide as a red, amorphous substance, which is insoluble in the usual organic

solvents, but crystallises from phenol in red, lustrous scales, and decomposes at about 230° ; its *sodium* and *silver* salts are described. The *acetyl* derivative crystallises in yellow, silky needles, and melts at 221° ; the *ethyl ether* forms yellow needles and melts at 173° .

When bromohydroxynaphthaphenazine is heated with benzyl chloride and sodium ethoxide, a compound, $C_{16}H_{10}ON_2$, is produced, which appears to be identical with that obtained from β -naphtheturhodole by Zincke (Abstr., 1893, i, 357) and regarded by him as an 'insoluble modification' of the eurhodole. By the action of nitric acid, bromohydroxynaphthaphenazine is converted into 5:6-diketonnaphthaphenazine (naphthaphenazine- β -quinone), and when treated with phenol and sulphuric acid yields 5-hydroxynaphthaphenazine (α -naphtheturhodole).

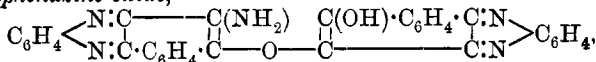
6-Anilino-5-hydroxy- $\alpha\beta$ -naphthaphenazine (6-anilino- α -naphtheturhodole), $OH \cdot C \cdot C_6H_4 \cdot C:N > C_6H_4$, obtained by the action of aniline on bromohydroxynaphthaphenazine, crystallises in red needles or leaflets, melts at $210-220^{\circ}$, is soluble in benzene, toluene, or glacial acetic acid, and dissolves in alcoholic alkali with formation of a violet solution; its *diacetyl* derivative melts at 226° .

Bromohydroxydinaphthaphenazine oxide,



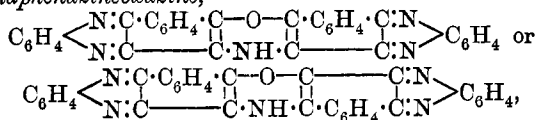
obtained by heating bromohydroxynaphthaphenazine with nitrobenzene, crystallises in brownish-violet needles, and melts at 300° ; when heated with sodium ethoxide, it is instantly converted into *dinaphthaphenazinefuran*, $C_6H_4 < \begin{array}{c} N:C \cdot C_6H_4 \cdot C \\ N:C \cdot C \end{array} \begin{array}{c} O \\ C \end{array} \begin{array}{c} C \\ C \cdot C_6H_4 \cdot C:N \end{array} > C_6H_4$, which crystallises from hot nitrobenzene in greenish-yellow needles, and melts above 300° .

When bromohydroxynaphthaphenazine is heated with alcoholic ammonia, it yields a substance which is either dihydroxydinaphthaphenazineimide, $NH \left(\begin{array}{c} C(OH) \cdot C_6H_4 \cdot C:N \\ C \end{array} > C_6H_4 \right)_2$, or *aminohydroxydinaphthaphenazine oxide*,



but more probably the latter; it crystallises in olive-green needles which contain $1H_2O$ and become blue when heated; it does not melt below 300° . The same compound is produced by the action of alcoholic ammonia on anilinohydroxynaphthaphenazine. The *ethyl* derivative, $NEt(C_{16}H_8N_2 \cdot OH)_2$ or $NHEt \cdot C_{16}H_8N_2 \cdot O \cdot C_{16}H_8N_2 \cdot OH$, obtained by heating the bromophenazine with alcoholic ethylamine, is an olive-green amorphous substance.

Dinaphthaphenazineoxazine,



produced when either of the two substances described in the last paragraph is heated with nitrobenzene or glacial acetic acid, crystallises in lustrous, dark-blue needles, and melts above 300°. E. G.

Reaction between Substituted Aminobenzophenones and Aromatic Amines in presence of Sulphuric Acid. By PAUL LEMOULT (*Compt. rend.*, 1901, 132, 885—888).—When tetramethyl-*p*-diaminobenzophenone and diphenylamine interact in presence of sulphuric acid, tetramethylphenyl-*p*-triaminotriphenylmethanesulphonic acid is obtained in almost theoretical quantity. A similar result is obtained with the tertiary methyl, ethyl, benzyl, and other substitution derivatives of diphenylamine, and with its homologues, such as phenyl-*p*-tolylamine or phenyl-*o*-tolylamine, but not with *p*-ditolylamine, or with any secondary or tertiary amine containing only one benzene nucleus. Phenyl- α -naphthylamine, phenyl- β -naphthylamine, *o*-tolyl- β -naphthylamine, and methylphenyl- β -naphthylamine give the reaction, but not *p*-tolyl- α -naphthylamine, *p*-tolyl- β -naphthylamine, or $\alpha\beta$ -dinaphthylamine.

In order that the condensation may take place it is essential that the amine contain at least one phenyl group, and that the para-position in the latter be unoccupied. The same condensation takes place between tetraethyl-*p*-diaminobenzophenone and diphenylamine, ethyl-diphenylamine, phenyl- α -naphthylamine, and phenyl β -naphthylamine, but not with *p*-ditolylamine, *p*-tolyl- α -naphthylamine, *p*-tolyl- β -naphthylamine, α -dinaphthylamine, β -dinaphthylamine, ethylaniline, and diethylaniline, or benzylaniline. Sulphonation of the benzophenone does not affect the reaction, although it has some influence on the exact colour of the product.

Dimethylaminobenzophenone and its sulphonic acid undergo a similar condensation, subject to the same limitations, and the products will be described subsequently.

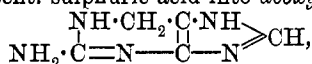
It will be seen that the condensation in presence of sulphuric acid is less general than in presence of phosphorus oxychloride, since in the latter case the nature of the amine has comparatively little influence on the occurrence and progress of the reaction. C. H. B.

Electrolytic Reduction of Xanthine. By JULIUS TAFEL and BENNO ACH (*Ber.*, 1901, 34, 1165—1169. Compare this vol., i, 106).—Xanthine, $C_5H_4O_6N_4$, is converted by electrolytic reduction into deoxyxanthine, $NH \cdot CH_2 \cdot C \cdot NH$
 $CO-NH \cdot C \rightarrow CH$, the yield being nearly quantitative when the reduction is carried out in 75 per cent. sulphuric acid below 12°. It crystallises with $1H_2O$ in needles, and is deposited from supersaturated solutions as an anhydrous granular powder, which gradually takes up water at 25° and is reconverted into needles. When heated above 250°, it gradually decomposes without melting. In general properties, it closely resembles the methyldeoxyxanthines and is probably 5-oxy-6:7-dihydropurine.

It is oxidised by silver nitrate, probably with formation of 5-hydroxypurine, and is also oxidised by potassium permanganate and lead peroxide. It dissolves in both acids and alkalis, the acid solutions

being easily decomposed by heat. *Deoxyxanthine sulphate* crystallises in colourless needles, the *nitrate* is a granular, crystalline powder, and the *picrate* crystallises in yellow, anhydrous needles. Phosphotungstic acid, phosphomolybdic acid, and copper sulphate all produce precipitates. A. H.

Reduction Products of Guanine. By JULIUS TAFEL and BENNO ACH (*Ber.*, 1901, **34**, 1170—1181. Compare the foregoing abstract).—Guanine, $C_5H_5ON_5$, is converted by electrolytic reduction in solution in 60 per cent. sulphuric acid into *deoxyguanine*,

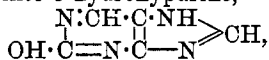


which crystallises in microscopic needles, and melts and decomposes at 204° . It is a strong base, which combines with atmospheric carbon dioxide and forms salts, both with one and two equivalents of mineral acids. The normal *sulphate*, $(C_5H_7N_5)_2\cdot H_2SO_4$, crystallises with $1H_2O$ in granules, and when anhydrous melts and decomposes at 267° . The *hydrogen sulphate*, $C_5H_7N_5\cdot H_2SO_4$, crystallises in yellowish, anhydrous prisms. The normal *hydrochloride* crystallises in tablets and dissolves in 16.9 parts of water at 0° . The solution gives precipitates with the usual reagents for basic substances. The acid hydrochloride has not been prepared pure. *Deoxyguanine acetate*, $C_5H_7N_5\cdot C_2H_3O_2$, crystallises in prisms, and melts and decomposes at about 222° . The *picrate* crystallises in orange yellow rhombohedra.

Deoxyguanine is converted by oxidation, which is best carried out by the action of bromine on the acetate in presence of acetic acid, into

5-aminopurine, $\begin{array}{c} \text{N}:\text{CH}\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{NH}_2\cdot\text{C}=\text{N}-\text{C}-\text{N} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{CH}$. The base crystallises with

$1H_2O$ in spherical aggregates, and is more readily soluble than the isomeric adenine, which it closely resembles in its general properties. It yields precipitates with mercuric chloride, phosphomolybdic acid, and cadmium chloride. It gives no colour reaction on exposure to air after treatment with zinc and hydrochloric acid, and can thus be readily distinguished from adenine. The base is soluble both in acids and alkalis; the *sulphate* is more readily soluble than adenine sulphate, the *nitrate* is sparingly soluble, the *platinichloride* is an amorphous precipitate, the *oxalate* crystallises in needles or granules, and the *picrate* crystallises without water in yellow needles. Nitrous acid converts aminopurine into 5-hydroxypurine,



which crystallises with $1H_2O$ in needles, becomes anhydrous at 122° , and dissolves in 22 parts of boiling water. On exposure to air after treatment with zinc and hydrochloric acid, followed by excess of alkali, it yields a red coloration similar to that produced by adenine and hypoxanthine. Baryta dissolves the compound at first, but the *barium* salt soon separates. The *nitrate* crystallises in hair-like needles; silver nitrate produces a gelatinous precipitate. A. H.

Tetrahydrouric Acid. By JULIUS TAFEL (*Ber.*, 1901, **34**, 1181—1184. Compare this vol., i, 236).—Tetrahydrouric acid is

converted by excess of aqueous baryta at 150° into $\alpha\beta$ -diaminopropionic acid. This confirms the view expressed previously, that the constitution of tetrahydrouric acid is not indicated by the formula $\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{NH}$
 $\text{CO}\cdot\text{NH}\text{---}\text{CH}\cdot\text{NH}>\text{CO}$, but more probably by the formula $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}<\text{CH}_2\cdot\text{NH}>\text{CO}$. The properties of $\alpha\beta$ -diaminopropionic acid were found, in some cases, to differ from those described by Klebs (Abstr., 1893, i, 686), the experiments being carried out with acid prepared by his method. The nitrate melts and decomposes at $191\text{--}193^{\circ}$ (Klebs, 170°), and the dibenzoyl derivative melts at $188\text{--}189^{\circ}$ (Klebs, $195\text{--}197^{\circ}$). A. H.

Syntheses in the Purine Group. By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1901, 34, 1234—1257).—5-Chloro-6-amino-4-methylpyrimidine, $\text{N}<\text{CH}=\text{N}>\text{C}(\text{NH}_2)\cdot\text{CCl}>\text{CMe}$, prepared by the action of chlorine on 6-amino-4-methylpyrimidine (Abstr., 1900, i, 55), crystallises from water in stout prisms, sinters at 195° , melts at $197\text{--}198^{\circ}$, volatilises slowly above 100° , and dissolves readily in acids and in hot alcohol or ether. The corresponding bromo-compound crystallises from hot water in long needles, melts at 197° , sublimes slowly at 100° , and gives a *platinichloride* which crystallises in orange-yellow needles.

6-Nitroamino-4-methylpyrimidine, $\text{C}_4\text{N}_2\text{H}_2\text{Me}\cdot\text{NH}\cdot\text{NO}_2$, prepared by the action of nitric acid on methylaminopyrimidine, crystallises from water in flat, colourless prisms, and on reduction is usually reconverted into methylaminopyrimidine. When reduced with zinc dust and acetic acid in presence of ice, it gives 6-hydrazino-4-methylpyrimidine, $\text{C}_4\text{N}_2\text{H}_2\text{Me}\cdot\text{NH}\cdot\text{NH}_2$, which crystallises from ethyl acetate in colourless needles, melts at $138\text{--}140.5^{\circ}$, reduces Fehling's solution, and distils without decomposition.

6-Nitroamino-2-chloro-4-methylpyrimidine, $\text{C}_4\text{N}_2\text{HMeCl}\cdot\text{NH}\cdot\text{NO}_2$, prepared by the action of nitric acid on 6-amino-2-chloro-4-methylpyrimidine, crystallises in minute needles, volatilises slowly at 100° , explodes on heating, and is reduced by hydrogen iodide and phosphorus to 6-amino-4-methylpyrimidine.

2 : 6-Dichloro-5-nitro-4-methylpyrimidine, $\text{C}_4\text{N}_2\text{MeCl}_2\cdot\text{NO}_2$, could not be obtained by nitrating dichloromethylpyrimidine, but was prepared by heating nitromethyluracil with phosphorus oxychloride at $155\text{--}160^{\circ}$ in sealed tubes; it distils at 240° , crystallises from light petroleum or from alcohol in stout prisms, and melts at $53\text{--}54.5^{\circ}$. 2-Chloro-5-nitro-6-amino-4-methylpyrimidine, $\text{NO}_2\cdot\text{C}_4\text{N}_2\text{MeCl}\cdot\text{NH}_2$, prepared by the action of alcoholic ammonia on the preceding compound, crystallises from alcohol in flat, reddish needles and melts at $170\text{--}171^{\circ}$. 2-Chloro-5 : 6-diamino-4-methylpyrimidine, $\text{C}_4\text{N}_2\text{MeCl}(\text{NH}_2)_2$, prepared by reducing the preceding compound with stannous chloride, crystallises from hot water in flat, glassy needles, melts at 250° , and forms a crystalline platini-chloride; reduction with hydriodic acid gives 5 : 6-diamino-4-methylpyrimidine, $\text{C}_4\text{N}_2\text{HMe}(\text{NH}_2)_2$, which crystallises from acetone in stout columns, melts at $208\text{--}209^{\circ}$ and boils without decomposition at

325—330°; the *platinichloride* forms square tablets, and the *hydriodide* colourless prisms. The *formyl* derivative, $\text{NH}_2 \cdot \text{C}_4\text{N}_2\text{HMe} \cdot \text{NH} \cdot \text{CHO}$, crystallises from alcohol in flat needles, and when heated above 200°

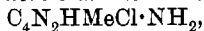
is converted into 7-methylpurine, $\begin{array}{c} \text{N} \cdot \text{CMe} : \text{C} \cdot \text{NH} \\ | \quad \quad | \\ \text{CH} \cdot \text{N} = \text{C} - \text{N} \end{array} \gg \text{CH}$, which sublimes readily, crystallises from toluene in silky needles, melts at 235—236°, and dissolves both in acids and alkalis; the *potassium* salt forms minute needles, the *picrate* is a crystalline powder, and the *platinichloride* forms yellow needles.

2-Oxy-7-methylpurine, $\begin{array}{c} \text{N} \cdot \text{CMe} : \text{C} \cdot \text{NH} \\ | \quad \quad | \\ \text{CH} \cdot \text{N} = \text{C} \cdot \text{NH} \end{array} \gg \text{CO}$, prepared by heating diaminomethylpyrimidine with carbamide at 170°, crystallises from alcohol in minute, snow-white needles, dissolves in hot water, and has no acid properties; the *hydrochloride* crystallises in needles, sinters at 325°, melts with frothing at about 345°, and is only slightly soluble in strong hydrochloric acid; the *aurichloride* forms golden-yellow needles or flat prisms. 2-Thio-7-methylpurine, prepared by heating diaminomethylpyrimidine with thiocarbamide, forms a colourless, crystalline powder, dissolves in ammonia and in alkalis, and volatilises on heating.

4-Methyl-5:6-aziminopyrimidine, $\begin{array}{c} \text{N} \cdot \text{CMe} : \text{C} \cdot \text{NH} \\ | \quad \quad | \\ \text{CH} \cdot \text{N} = \text{C} - \text{N} \end{array} \gg \text{N}$, prepared by the action of nitrous acid on diaminomethylpyrimidine, crystallises from hot water in colourless, microscopic needles, sinters at 160° and melts at 174° to a red liquid.

By heating diaminomethylpyrimidine with benzil at 170°, the *azine*, $\begin{array}{c} \text{N} \cdot \text{CMe} : \text{C} \cdot \text{N} : \text{CPh} \\ | \quad \quad | \\ \text{CH} \cdot \text{N} = \text{C} \cdot \text{N} : \text{CPh} \end{array}$, is formed; it crystallises from hot alcohol in yellow prisms, sinters at about 180° and melts at 184°.

2:6-Dichloro-5-nitro-4-methylpyrimidine is reduced by boiling with zinc dust and water to 2-chloro 5-amino-4-methylpyrimidine,



which melts at 92° and separates from water in felted needles. Sodium methoxide converts it into 5-amino-2-methoxy 4-methylpyrimidine, $\text{OMe} \cdot \text{C}_4\text{N}_2\text{HMe} \cdot \text{NH}_2$, which melts at 88—89·5°, and has an odour suggestive of lobsters. 5-Amino-4-methylpyrimidine, $\text{C}_4\text{N}_2\text{H}_2\text{Me} \cdot \text{NH}_2$, prepared by reducing the chloro-derivative with hydriodic acid, separates from benzene in flat crystals, melts at 152—153°, and boils at about 260°; it forms a *hydrochloride*, a *platinichloride* crystallising in oblong prisms, and an *aurichloride* crystallising in flat needles. 2:5-Diamino-4-methylpyrimidine, $\text{C}_4\text{N}_2\text{HMe}(\text{NH}_2)_2$, prepared by heating 2-chloro-5-amino-4-methylpyrimidine with alcoholic ammonia at 200—215°, crystallises from ethyl acetate in short prisms, melts at 183—184°, and is a weaker base than the two isomerides.

2:6-Diamino-4-methylpyrimidine, formed as a bye-product in the action of ammonia on 2:6-dichloro-4-methylpyrimidine (Abstr., 1900, i, 54), crystallises from water in clear needles with $1\text{H}_2\text{O}$, and from acetone in glassy needles containing acetone; it melts at 183—185° and boils at 305—308°.

5-Nitro-2:6-diamino-4-methylpyrimidine, $\text{NO}_2 \cdot \text{C}_4\text{N}_2\text{Me}(\text{NH}_2)_2$, pre-

pared by the action of nitric and sulphuric acids on the preceding compound, crystallises from acetic acid, alcohol, or water, forms yellow prisms or needles, melts at $232-233^{\circ}$, and can also be prepared by the action of ammonia on 2:6-dichloro-5-nitro-4-methylpyrimidine. It is reduced by stannous chloride to 2:5:6-triamino-4-methylpyrimidine, $C_4N_3Me(NH_2)_3$, which crystallises from water in colourless, glistening needles, from alcohol in stout prisms or rhombohedra, melts at 243° , and reduces Fehling's solution; the *hydrochloride* crystallises in needles, the *platinichloride* in flat, lemon-yellow prisms, and the *picrate* forms a crystalline powder. The *formyl* derivative forms minute, felted needles, and when heated at 300° is converted into 5-amino-7-methyl-

purine, $NH_2 \cdot \overset{\overset{N \cdot CMe \cdot C \cdot NH}{\parallel}}{C} - N : \overset{\overset{N \cdot CMe \cdot C \cdot NH}{\parallel}}{C} - N \gg CH$, which crystallises from water in felted, silky needles, volatilises when heated on a watch glass, melts above 300° when heated in a capillary tube, and gives a crystalline *hydrochloride*, *platinichloride*, *aurichloride*, *dichromate*, *ferrocyanide*, and *picrate*.
T. M. L.

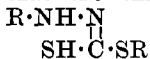
Reduction of Nitro-azo-colouring Matters. By AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1901, 132, 985—988).—The substantive colouring matter produced by the action of diazotised *m*-azoxy-*o*-toluidine on 1-naphthol-4-sulphonic acid is more conveniently prepared by reducing 4-nitrotoluene-2-azo-1-naphthol-4-sulphonic acid in an alkaline solution by means of stannous oxide, arsenious acid, formaldehyde, or dextrose, the yield obtained by the use of the last of these reagents being quantitative. During reduction, the temperature must be kept below 60° , otherwise an azodiamine is produced. 3-Azo-2-toluidine, $N_2(C_6H_3Me \cdot NH_2)_2$, prepared in this manner, crystallises from alcohol, ether, or benzene in brown needles, and melts at $218-220^{\circ}$.
G. T. M.

Oxidation of Symmetrical Secondary Benzylhydrazines to Hydrazones. By THEODOR CURTIUS and H. PAULI (*Ber.*, 1901, 34, 847—853).—*o*-Chlorobenzaldazine, $C_6H_4Cl \cdot CH : N : N : CH \cdot C_6H_4Cl$, crystallises from alcohol in glistening, yellow needles and melts at 143.5° . It is reduced by sodium amalgam to *s*-di-*o*-chlorobenzylhydrazine, $N_2H_2(CH_2 \cdot C_6H_4Cl)_2$, which crystallises from alcohol in small, colourless needles and melts at $86-87^{\circ}$; the *hydrochloride*, $C_{14}H_{14}N_2Cl_2 \cdot HCl$, crystallises from dilute hydrogen chloride in glistening, colourless needles and melts at 169° ; the *picrate* forms glistening, yellow needles, and melts and decomposes at 144° ; the *diacetyl* derivative, $C_{18}H_{18}O_2N_2Cl_2$, separates from alcohol in colourless crystals and melts at 102° ; the *dibenzoyl* derivative, $C_{28}H_{22}O_2N_2Cl_2$, separates from alcohol in hard crystals and melts at 118° . The *dinitroso*-derivative, $N_2(NO)_2(CH_2 \cdot C_6H_4Cl)_2$, separates from ether as a yellow, crystalline mass and melts at $50-51^{\circ}$; by warming with alcohol, it is converted into *o*-chlorobenzylidenenitroso-*o*-chlorobenzylhydrazine, $C_6H_4Cl \cdot CH_2 \cdot N(NO) \cdot N : CH \cdot C_6H_4Cl$, which separates in yellow needles and melts and decomposes at $100-101^{\circ}$. *o*-Chlorobenzylhydrazine *hydrochloride*, $C_6H_4Cl \cdot CH_2 \cdot NH \cdot NH_2 \cdot HCl$, prepared by hydrolysing the preceding compound with dilute hydrogen chloride, separates from

alcohol in colourless, glistening crystals and melts at 146° ; it condenses with *o*-chlorobenzaldehyde in presence of a few drops of sulphuric acid to form *o*-chlorobenzylidene-*o*-chlorobenzylhydrazine, $C_6H_4Cl \cdot CH_2 \cdot NH \cdot N : CH \cdot C_6H_4Cl$, which crystallises from alcohol in small, yellow needles and melts at $83-84^{\circ}$. Nitroso-*o*-chlorobenzylhydrazine, $C_6H_4Cl \cdot CH_2 \cdot N(NO) \cdot NH_2$, crystallises from warm water or from dilute alcohol in glistening, colourless flakes and melts at 57° ; it condenses with *o*-chlorobenzaldehyde to form *o*-chlorobenzylidenenitroso-*o*-chlorobenzylhydrazine, and with benzaldehyde to benzylidenenitroso-*o*-chlorobenzylhydrazine, $C_6H_4Cl \cdot CH_2 \cdot N(NO) \cdot N : CH \cdot C_6H_5$, which separates from alcohol in small, yellow crystals and melts and decomposes at $85-86^{\circ}$; the acetyl derivative, $C_{16}H_{14}ON_2Cl_2$, of the preceding compound separates from alcohol in colourless tablets and melts at 110° .

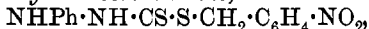
T. M. L.

Stereoisomerism of the Hydrazones of the Esters of Dithiocarbonic Acid. By MAX BUSCH (*Ber.*, 1901, 34, 1119-1127. Compare Busch and Lingenbrink, *Abstr.*, 1900, i, 66, 411).—The esters of phenyldithiocarbazinic acid, $NHPh \cdot NH \cdot CS \cdot SR$, when acted on by alkali, undergo intramolecular change into hydrazones of dithiocarbonic acid, $NHPh \cdot N : C(SH) \cdot SR$, which are readily converted into the corresponding dialkyl esters, $NHPh \cdot N : C(SR) \cdot SR'$. When R and R' are different radicles, these compounds should, in the light of Hantzsch's theory, exist in two stereoisomeric modifications. Such esters have now been obtained crystalline, and it is found that the two stereoisomerides can be obtained by varying the order in which the radicles R and R' are introduced into the compounds. Since the esters of carbazinic acid pass readily into diazole derivatives, it is assumed that the thialkyl group in them occupies the anti-position, thus:



The stereoisomeric hydrazones show no differences in their chemical behaviour, whilst the solubilities and melting points are approximately the same; the crystalline forms and the colours differ, however, to such an extent as to make it quite easy to recognise and separate any pair of isomerides. The separate isomerides are not readily converted one into the other, although such conversion can be brought about by long continued heating above the melting point; in general, equilibrium is attained after about an hour's heating, a mixture of the two forms being in all cases obtained.

p-Nitrobenzyl phenyldithiocarbazinate,

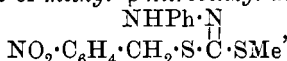


obtained by the action of the potassium salt on *p*-nitrobenzyl chloride, melts at 134° and crystallises from alcohol in faintly yellow, stout needles, from a mixture of benzene and light petroleum in small, white needles, and from chloroform in stout prisms; it is soluble in ether and to a very slight extent in light petroleum. Its alcoholic solution is turned red or brownish-red by alkali hydroxide or carbonate. Together with the above compound, a small quantity of the phenylhydrazone of di-*p*-nitrobenzyl dithiocarbonate, $NHPh \cdot N : C(S \cdot CH_2 \cdot C_6H_4 \cdot NO_2)_2$, is obtained; it separates from acetic acid in sparkling, scarlet, spear-

head shaped crystals, which melt at 148° and dissolve readily in chloroform.

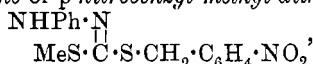
o-Nitrobenzyl phenyldithiocarbazinate, $C_{14}H_{13}O_2N_3S_2$, is readily soluble in chloroform, ether, or benzene, less so in alcohol, and crystallises in pale yellow or white crystals melting at 142° . The alcoholic solution is coloured dark red by alkali hydroxide or carbonate. The phenylhydrazone of di-*o*-nitrobenzyl dithiocarbonate forms a felted mass of very slender, sparkling, golden needles melting at $94-95^{\circ}$.

The phenylhydrazone of methyl *p*-nitrobenzyl dithiocarbonate,



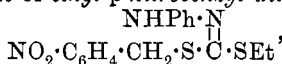
prepared from *p*-nitrobenzyl chloride and phenyl methyl dithiocarbazinate, crystallises from alcohol in bundles of sparkling, orange-red needles or prisms melting at 84° , and is readily soluble in chloroform.

The phenylhydrazone of *p*-nitrobenzyl methyl dithiocarbonate,



obtained from methyl iodide and *p*-nitrobenzyldithiocarbazinate, forms slender, lemon-yellow, silky needles melting at $89-90^{\circ}$. This form predominates in the mixture obtained by heating either of these two isomerides for an hour in a water-bath.

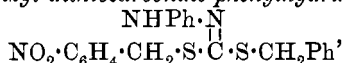
The phenylhydrazone of ethyl *p*-nitrobenzyl dithiocarbonate,



crystallises from a mixture of alcohol and ether in large, sparkling, scarlet prisms melting at 75° , and is readily soluble in benzene, chloroform, or ether and less so in alcohol. The isomeric phenylhydrazone of

p-nitrobenzyl ethyl dithiocarbonate, $\begin{array}{c} \text{NHPH} \cdot \text{N} \\ | \\ \text{EtS} \cdot \text{C} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{array}$, separates from alcohol in silky, lemon-yellow needles which soften at about 40° and melt at 42° . In solubility, it differs but very slightly from its isomeride.

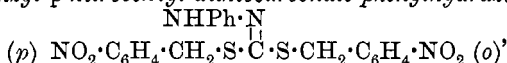
Benzyl *p*-nitrobenzyl dithiocarbonate phenylhydrazone,



forms shining, orange leaflets or flat needles melting at 98° and dissolves readily in chloroform. Its isomeride, *p*-nitrobenzyl benzyl dithiocarbonate

phenylhydrazone, $\begin{array}{c} \text{NHPH} \cdot \text{N} \\ | \\ \text{CH}_2\text{Ph} \cdot \text{S} \cdot \text{C} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{array}$, forms large, glassy, orange-yellow, flat needles which soften at about 101° and melt at 103° . When heated for an hour at $110-120^{\circ}$, either of these isomerides yields approximately equal quantities of the two forms.

o-Nitrobenzyl *p*-nitrobenzyl dithiocarbonate phenylhydrazone,



obtained from *p*-nitrobenzyl chloride and *o*-nitrobenzyl dithiocarbazinate, crystallises from a mixture of alcohol and ether in shining, many faced, garnet-red prisms melting at 81° , and dissolves readily in chloroform. The isomeric *p*-nitrobenzyl *o*-nitrobenzyl dithiocarbonate,

$\text{NHPh} \cdot \text{N} \begin{smallmatrix} \text{H} \\ | \end{smallmatrix}$

(o) $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{S} \cdot \text{C} \begin{smallmatrix} \text{H} \\ | \end{smallmatrix} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ (p), separates from alcohol in long, orange to orange-red needles melting at 107° .

Unlike similar compounds with lower substituent radicles, the hydrazones described above are not capable of yielding salts with acids. With concentrated sulphuric acid they yield an emerald green colour, excepting those containing two benzyl residues, which give a bluish-green coloration; in both cases, the colour changes to yellow on heating.

T. H. P.

Benzeneazopyrroles. By GIUSEPPE PLANCHER and E. SONCINI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 299—303).—Phenylcarbimide is found to react with benzeneazopyrrole and with benzenazo-2:4-dimethylpyrrole, both of which have the azo-group in the 2-position in the pyrrole nucleus, but no action takes place with either benzenazo-2:5-dimethylpyrrole or benzenazo-2-phenyl-5-methylpyrrole in which the azo-group occupies the 3-position. This would seem to indicate, not necessarily that the 3-benzeneazopyrroles are in the free state true azo-compounds and that the benzeneazopyrroles are really hydrazones, but that the 2-compounds are capable of acting in the tautomeric form in the presence of phenylcarbimide whilst the other derivatives are not. It is possible that the capability of reaction of the 2-compounds is due to the proximity of the imino-group of the phenylhydrazine residue to the basic nitrogen atom of the pyrrole nucleus.

Perfectly dry phenylcarbimide does not react with pyrrole, 2:5-dimethylpyrrole, 2:4-dimethylpyrrole, 5-phenyl-2-methylpyrrole, carbazole, succinimide, or iodole, either in the cold or on heating in the water-bath in presence of light petroleum.

Benzeneazopyrrole and phenylcarbimide yield a compound, $\text{C}_{17}\text{H}_{14}\text{ON}_4$, separating from light petroleum in yellowish-red needles melting at $108\text{--}110^\circ$.

Benzenazo-2:4-dimethylpyrrole, $\text{C}_{12}\text{H}_{13}\text{N}_3$, separates from dilute alcohol in pale, garnet-red crystals melting at $118\text{--}119^\circ$. With phenylcarbimide it gives an unstable compound, $\text{C}_{19}\text{H}_{18}\text{ON}_4$, which melts at $70\text{--}71^\circ$ and is readily resolved into its components.

Benzenazo-2:5-dimethylpyrrole, already prepared by Fischer, who did not analyse it, and gave its melting point as 124° , has been prepared pure and analysed; its melting point is found to be 135° . It is a very stable, pale yellow compound, and does not react with phenylcarbimide.

Benzenazo-2-methyl-5-phenylpyrrole was prepared and analysed. It is an orange-yellow compound which melts and decomposes at 120° with previous softening, and does not react with phenylcarbimide.

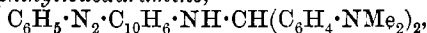
Tetrabromopyrrole, prepared but not analysed by Hepp, has been obtained by the authors, and has the composition C_4HNBBr_4 .

T. H. P.

Characterisation of Aminoazo-compounds. By RICHARD MÖHLAU and MAX HEINZE (*Ber.*, 1901, 34, 881—888).—*Benzazophenyl-leucauramine*, $\text{N}_2\text{Ph} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, prepared by the

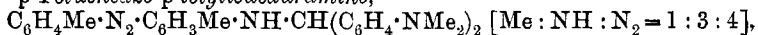
action of tetramethyldiaminobenzhydrol on *p*-aminoazobenzene, separates from a mixture of benzene and light petroleum in brownish-yellow prisms, melts at 156.5°, is slowly hydrolysed again by dilute acids, and gives acetyl-*p*-aminoazobenzene by the action of acetic anhydride and sodium acetate. Dimethylaminoazobenzene does not react with the benzhydrol.

Benzazo-α-naphthylleucauramine,

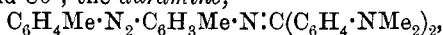


prepared from benzazo-α-naphthylamine and the benzhydrol, crystallises in yellowish-brown prisms, melts at 234–235°, and is decomposed like the preceding compound by dilute acids and by acetic anhydride.

p-Tolueneazo-p-tolylleucauramine,

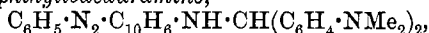


prepared from *o*-azo-*p*-aminotoluene and the benzhydrol at temperatures below 40°, separates from a mixture of benzene and light petroleum in ruby-red needles and melts at 174.5°. When the action takes place between 40° and 80°, the *auramine*,



is formed, and this is also produced by heating an alcoholic solution of the leucauramine; it crystallises from a mixture of benzene and light petroleum in orange-yellow flakes, melts at 190°, and is hydrolysed by mineral acids to *o*-azo-*p*-aminotoluene and tetramethyldiaminobenzophenone.

Benzazo-β-naphthylleucauramine,



prepared from benzazo-β-naphthylamine and the benzhydrol at temperatures below 40°, crystallises from hot acetone in scarlet needles and melts at 184°; by boiling an alcoholic solution of the leucauramine, a compound, $\text{C}_{33}\text{H}_{31}\text{N}_5$, is produced which melts at 74°, but is, perhaps, not the corresponding auramine, since tetramethyldiaminobenzophenone could not be found amongst the products of hydrolysis. T. M. L.

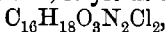
Formation of Acetone from Albumin. By FERDINAND BLUMENTHAL and CARL NEUBERG (*Chem. Centr.*, 1901, i, 788; from *Deut. med. Woch.*, 27, 6–7).—Albuminous substances have been found to yield acetone when oxidised by means of iron salts. By digesting gelatin with hydrogen peroxide and a saturated solution of ferrous sulphate, acetone and an aldehyde are formed. The presence of the former is readily detected by Stock's method; to the distillate after treating with sodium hydroxide solution, hydroxylamine, and pyridine, ether is added and then bromine until the ethereal layer becomes yellow. On adding hydrogen peroxide, the yellow coloration becomes blue if acetone is present and by this means 1 part of acetone in 5000 of water can be detected. The aldehyde has not yet been examined. E. W. W.

Ichthulin from the Cod. By P. A. LEVENE (*Zeit. physiol. Chem.*, 1901, 32, 281–284).—Ichthulin from the roe of the cod differs but very little in composition from the ichthulin obtained by Walter from carp roe (*Abstr.*, 1891, 1389). When hydrolysed, however, it does not yield a sugar with reducing properties, and on treatment with alkalis gives *ichthulic acid* (C, 32.56; H, 6.0; N, 14.03; S, 0.146,

and P, 10.34) which is very similar to vitellic acid (this vol., i, 300). Ichthulin from the cod resembles vitellin more than it does Walter's ichthulin.

J. J. S.

Reduction Products and Constitution of Hæmin. By MARCELLUS NENCKI and J. ZALESKI (*Ber.*, 1901, 34, 997—1010. Compare Abstr., 1896, ii, 335; 1900, i, 709).—*Mesoporphyrin*, $C_{16}H_{18}O_2N_2$, is obtained in the form of its *hydrochloride*, $C_{16}H_{18}O_2N_2 \cdot HCl$ when crude acetylhaemin is reduced with hydriodic acid of sp. gr. = 1.7 and glacial acetic acid and finally with phosphonium iodide, and the product crystallised several times from dilute hydrochloric acid; the *base* forms a minutely crystalline, red coloured mass, and in its properties resembles hæmatoporphyrin. It is insoluble in water, and very sparingly soluble in alcohol or ether, but dissolves readily in alkalis, and does not melt at 340° . Its hydrochloride is decomposed by water, and its solutions, whether neutral, alkaline, or acid, appear to be identical spectroscopically with those of hæmatoporphyrin. When oxidised in hydrochloric acid solution with hydrogen peroxide, it yields a green compound,



probably chlorohæmatoporphyrin hydrochloride, $C_{16}O_{17}O_3N_2Cl \cdot HCl$.

A bye-product obtained in the preparation of mesoporphyrin is a volatile oil *hæmopyrrole*, $CHMeEt \cdot C \begin{smallmatrix} \text{CH} \cdot \text{NH} \\ \text{CH} : \text{CH} \end{smallmatrix}$ or $\begin{smallmatrix} \text{CMe} : \text{CH} \\ \text{CPr} = \text{CH} \end{smallmatrix} \text{NH}$.

With mercuric chloride, it yields a *compound*, $(C_8H_{12}N)_2Hg \cdot 4HgCl_2$, sintering at 70° , and soluble in alcohol but insoluble in water. Its *picrate*, $C_8H_{13}N \cdot C_6H_3O_7N_2$, crystallises from benzene in needles, melts at 108° , and decomposes at 125° .

When exposed to the air, the pyrrole base turns red, yielding urobilin, and when taken into the animal system it is also excreted in the form of urobilin.

J. J. S.

Constitution of Thymine. By H. STEUDEL (*Zeit. physiol. Chem.*, 1901, 32, 241—244. Compare Abstr., 1900, i, 467, and this vol., i, 108).—Details for the preparation of nitrothymine are given. When oxidised with barium permanganate, thymine yields a considerable amount of carbamide.

As a result of these and of the previous investigations, thymine is regarded as 5-methyl-2 : 6-dioxypyrimidine, $CMe \begin{smallmatrix} \text{CH} \cdot \text{NH} \\ \text{O} \cdot \text{NH} \end{smallmatrix} \text{CO}$.

The compound, $C_4H_4O_2N_2$, described by Ascoli (this vol., i, 108) is probably 2 : 6-dioxypyrimidine.

J. J. S.

Paranucleic Acid from Casein. I. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1901, 32, 245—267).—An *iron* derivative of paranucleic acid is obtained when casein is digested with pepsin, the product evaporated, neutralised, and boiled with a 5 per cent. solution of iron alum. The average composition is C, 31.9; H, 4.43; N, 9.72; P, 2.55, and Fe, 21.87 per cent. It dissolves readily in moderately strong hydrochloric or in acetic acid, but is precipitated on dilution. It is also soluble in dilute sodium carbonate or hydroxide and also in aqueous ammonia, but is decomposed by concentrated sodium hydroxide, yielding ferric hydroxide and a solution which gives a precipitate when warmed

with barium chloride solution. The liver of animals fed for 10 days on this iron compound becomes rich in iron; in some cases, it contains three times as much as was originally present.

Paranucleic acid is obtained when the iron compound is decomposed with sodium hydroxide and acidified with acetic acid; it is then converted into its *copper* derivative and this decomposed with hydrogen sulphide. The acid is readily soluble in water, but insoluble in alcohol or acetic acid. Its solutions are lævorotatory $[\alpha]_D - 46^\circ$ (approx.), and give a precipitate when warmed with barium chloride solution. The acid is decomposed when boiled with sodium hydroxide of sp. gr. 1.34, yielding orthophosphoric acid. It gives precipitates with a hot solution of iron alum, mercuric chloride, copper acetate, lead acetate, tannin, phosphotungstic acid, saturated ammonium sulphate, or dilute egg-albumin. It also gives the biuret and xanthoprotein colour tests.

J. J. S.

Coagulating Action of Papayotin on Solutions of Peptone. By D. KURÁČEFF (*Chem. Centr.*, 1901, i, 788; from *Centr. med. Wiss.*, 1901, 39, 145—147. Compare Okuneff and Lawroff, *Zeit. physiol. Chem.*, 26, 513; Zawialoff, *Diss. Dorpat*, 1899).—When a solution of papayotin is added to a 10—18 per cent. solution of Witte's peptone which has been rendered alkaline by means of sodium carbonate and the mixture then digested at 40° for an hour, a flocculent precipitate is formed. By heating with alkalis, the precipitate becomes gelatinous and by the action of papayotin solutions on solutions containing more than 20 per cent. of peptone, gelatinous products are obtained. The papayotin acts as a ferment, for solutions which have been boiled are inactive. Solutions of caseoses and of the peptic products of muscle albumin are also attacked by papayotin.

E. W. W.

Protoplasm and Enzymes. By THOMAS BOKORNY (*Pflüger's Archiv*, 1901, 85, 257—270. Compare this vol., i, 177).—Chemical investigations on enzymes, so far as such have been possible, have shown that they are proteid or proteid-like in nature. Many, in fact, appear to be nucleo-proteid. Nucleo-proteid is also the main constituent of protoplasm. The similarity between protoplasm and enzymes is, indeed, very close. The action of acids, alkalis, antiseptics, and numerous other reagents, the influence of temperature and other agents, are all shown to be similar in both cases.

W. D. H.

Catalase, a New Enzyme of General Occurrence, with Special Reference to the Tobacco Plant. By OSCAR LOEW (*U.S. Dept. Agr., Rep.*, No. 68, 1901, pp. 47).—Catalase occurs in an insoluble (α -catalase) and in a soluble form (β -catalase), the former being probably a compound of β -catalase with a nucleo-proteid, whilst the latter is an albumose, and can be liberated from α -catalase by the action of very dilute alkali. The enzyme was found in every vegetable tested for it; leaves contain mainly α -catalase, whilst in seeds β -catalase predominates.

Both forms resist the effects of time longer than ordinary oxydases.

β -Catalase loses its power in aqueous solutions free from bacteria, and is killed by heating the solution at 71 — 75° ; somewhat higher tem-

peratures are required in very weak alkali solutions, and a lower temperature suffices in slightly acidified solutions. The temperature at which α -catalase is killed is about the same.

Mechanical motion greatly increases the action of catalase on hydrogen peroxide. Aqueous extracts of sweated tobacco (20 c.c.) mixed with hydrogen peroxide (10 c.c.) gave off 24 and 51 c.c. of oxygen respectively when left untouched and violently agitated.

Potassium nitrate (10 per cent.) has a very marked effect on depressing the activity of β -catalase, although the enzyme itself does not seem to be materially injured. Potassium salts retard the action more than sodium salts, and nitrates retard more than chlorides, sulphates, and carbonates. Even 3 per cent. solutions of anhydrous sodium carbonate attack β -catalase very slowly. Sodium fluoride (2 per cent.) and potassium oxalate (5 per cent.) cause no injury in twenty-four hours; and potassium thiocyanate and thiourea (5 per cent. solutions) seem to have no injurious effect on β -catalase, although they interfere with the action on hydrogen peroxide. Mercuric chloride is highly injurious.

Whilst highly dilute acids retard the action of α - and β -catalase, addition of 1 per cent. sodium carbonate to 10 c.c. of tobacco extract and 10 c.c. of hydrogen peroxide accelerated the evolution of oxygen. Acetic acid (0.1 per cent.) had no injurious effect in 1 hour, but gradually retarded the action at 35°. Sulphuric acid (2 per cent.) destroyed the catalytic power in 15 minutes; saturated baryta water kills β -catalase in two days, but α -catalase is more resisting. Absolute alcohol exerts no effect in twenty-four hours; even boiling absolute alcohol does not instantly kill the enzyme. Chloroform and ether in small amounts are without any marked effect. Phenol (1 per cent.) retards the action of the enzyme. Loss of activity occurs in presence of formaldehyde and of nitrous acid, indicating that labile amino-groups are concerned in the activity of the enzyme. Hydrogen cyanide readily kills β -catalase, whilst α -catalase shows considerable resistance. Hydrogen sulphide is injurious to α -catalase at the ordinary temperature, but the action is slow (compare Schönbein, *J. pr. Chem.*, 1863, 340); a good deal of sulphur is liberated. Hydroxylamine destroyed the soluble enzyme, but only retarded the action of the insoluble portion. Phenylhydrazine seems to form a still somewhat active compound with β -catalase; it reduces the activity of α -catalase. Alkaline silver solutions produced no effect on α -catalase; freshly precipitated silver oxide only had a moderate retarding effect on β -catalase.

Catalase is present in fungi in relatively very large amounts, and is produced by various bacteria (as, for instance, *Bacillus pyocyaneus*), the amount depending to some extent on the conditions of nutrition. It occurs in aqueous extracts of spleen, liver, brain, muscle, &c., but not in urine; also in infusoria, insects, worms, and molluscs.

The question whether catalase is an oxidising enzyme is discussed. α - and β -Catalase do not show a blue reaction with guaiacum, and do not produce the indophenol reaction; they have, however, the power of oxidising quinol.

As regards the physiological importance of catalase, it is suggested

that its function may be to prevent any accumulation of hydrogen peroxide. In the case of yeast, it may be of importance for the action of Buchner's zymase.

The universal occurrence of catalase is sufficient proof that the statements of Clermont, Wurster, Bach, and E. Baumann, that hydrogen peroxide may occur in living cells, are incorrect. N. H. J. M.

Commercial Preparations of Diastase. By GEORG BARTH (*Zeit. angew. Chem.*, 1901, 14, 368—371).—Using Lintner's method (Abstr., 1886, 386), the fermenting power of commercial preparations of diastase from eight different sources was estimated. The rapidity with which starch paste was clarified by the diastase was also tested. The details of the procedure in both these determinations are described in the paper. Five of the eight preparations exhibited little, if any, fermenting power; at the same time, they contained much starch, dextrin and reducing sugar and little nitrogen. Of the other three, Merck's diastase was a malt diastase, and had a fermenting power of 11.5 (on Lintner's standard); Witte's diastase was of animal origin and possessed a fermenting power of 27.4; Taka-diastase, obtained from the spores of certain moulds, exhibited a fermenting power of 8.63. K. J. P. O.

Properties of Galactase, a Digestive Ferment of Milk. By S. MOULTON BABCOCK, H. L. RUSSELL and ALFRED VIVIAN (15th *Ann. Rep. Agr. Expt. Stat. Univ. Wisconsin*, for 1897—1898, 77—86. Compare Abstr. 1900, i, 712).—Galactase rapidly decomposes hydrogen peroxide. The optimum temperature of galactase, as indicated by digestive experiments with milk, seems to be between 37° and 42°. In experiments with milk, it was found that the enzyme is destroyed by exposure for 10 minutes to a temperature of 76° and its activity was reduced by heating for the same period at 70°. Experiments with gelatin showed that a reaction neutral or slightly alkaline to litmus is most favourable to the liquefaction of gelatin; decinormal acid and alkali solutions retarded the action.

As regards the effect of heat on the hydrogen peroxide test for galactase, it was found that decomposition always took place under conditions of neutrality or alkalinity when the temperature did not exceed 75° for 1 hour, and 80° for 10 minutes. The amounts of galactase were higher than in Storch's experiments with milk (40th *Rep. Copenhagen Expt. Stat.*).

Acid, especially hydrochloric, materially retards the activity of galactase, indicating that the enzyme belongs to the tryptic rather than to the peptic type. Mercuric chloride, formalin, phenol and its derivatives, and carbon disulphide destroy the enzyme.

The prolonged action of galactase on milk results in the formation of decomposition products of protein, ranging from albumoses to ammonia, with tyrosine, leucine, and other intermediate products.

N. H. J. M.

Action of Chemical Agents on Yeast and on the Enzymes obtained from it. By THOMAS BOKORNY (*Chem. Zeit.*, 1901, 25, 365—366).—Various substances which completely kill the yeast cell do not destroy the fermentative functions of invertase; for example,

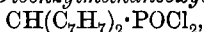
8 days' contact with absolute alcohol, 1 day with 5 per cent. formaldehyde, 1 day with chloroform, 16 days with 1 per cent. phenol. Twenty-four hours' contact with 0.2 per cent. acetic acid destroys the active properties of zymase, but even a 1 per cent. acid affects neither invertase nor maltase. Sixteen hours' contact with 0.5 per cent. sulphuric acid kills beer yeast, but not the mould forms of yeast ("Kahmhefe"). The enzymes are not so readily destroyed by sulphuric acid with the exception of zymase, which loses all its active properties after 24 hours' contact with 0.5 per cent., but not with 0.1 per cent. sulphuric acid. Alkalis (sodium hydroxide) also destroy the yeast protoplasm more readily than they do the enzymes.

Maltase is much more readily destroyed than invertase, in fact almost as readily as yeast protoplasm by most reagents. A 0.5 per cent. solution of oxalic acid, however, completely destroys the cell after 24 hours' contact but leaves the maltase intact. J. J. S.

Action of Invert Sugar on the Inversion of Sucrose by Sucrase. By VICTOR HENRI (*Compt. rend. Soc. Biol.*, 1901, 53, 288—290, 290—292).—The rapidity of the inversion of sucrose by the invertase of yeast is lessened by the addition of invert sugar (dextrose and lævulose); it is accelerated if more sucrose is added during the process. Tables showing the quantitative relations are given. W. D. H.

Philothion. By G. COSSETTINI (*Chem. Centr.*, 1901, i, 789; from *Boll. Chim. Farm.*, 40, 75—76. Compare de Rey-Pailhade, *Abstr.*, 1888, 1101; 1894, ii, 206).—When philothion is sterilised by filtering through a Chamberland filter, it loses its power of forming hydrogen sulphide from sulphur in cold solutions. E. W. W.

Dibenzylmethane- and Hydroxymethylenecamphor-phosphinic Acids. By AUGUST MICHAELIS and A. FLEMMING (*Ber.*, 1901, 34, 1291—1300).—The substance $C_{15}H_{17}O_3P$, obtained by Graebe (*Abstr.* 1875, 457) by the action of hydriodic acid and amorphous phosphorus on dibenzyl ketone, is dibenzylmethanephosphinic acid, $CH(C_6H_5)_2 \cdot PO(OH)_2$. When this acid is strongly heated, it decomposes with formation of dibenzylmethane and a little toluene. *Tetra-nitro-* and *dinitro-dibenzylmethane* crystallise from chloroform in white needles and melt at 162—164° and 139° respectively. The *aniline* salt of dibenzylmethanephosphinic acid, $CH(C_6H_5)_2 \cdot PO(OH) \cdot ONH_2Ph$, melts at 126°, and the *phenylhydrazine* salt at 148—149°; the *disilver* salt was also prepared. *Dibenzylmethaneoxychlorophosphine*,



obtained by heating the acid (1 mol.) with phosphorus pentachloride (2 mols.) is a thick, colourless liquid which boils at 228° under 20 mm. pressure, has a sp. gr. 1.036 at 15°, and by the action of water is readily converted into the acid. Dibenzylmethanephosphinic *anhydride*, $CH(C_6H_5)_2 \cdot PO_2$, obtained by heating equivalent quantities of the acid and the oxychlorophosphine in benzene solution, forms white, tabular crystals and melts at 151°. The *anilide*, $CH(C_6H_5)_2 \cdot PO(NHPh)_2$, crystallises in white needles and melts at 196°. The *phenylhydrazide*, $CH(C_6H_5)_2 \cdot PO(NH \cdot NHPh)_2$, melts at 164°. The *diethyl* ester boils at 240° under 20 mm. pressure; the *diphenyl* ester crystallises in hard,

white prisms and melts at 120° , and the *ditolyl* ester melts at 131° . *Dibenzylmethanephosphinamic acid*, $\text{CH}(\text{C}_7\text{H}_7)_2 \cdot \text{PO}(\text{OH}) \cdot \text{NH}_2$, obtained by the action of strong aqueous ammonia on the oxychlorophosphine, crystallises in lustrous, white leaflets, sinters at 230° , and melts at 244° ; its *silver* salt is described.

Hydroxymethylenecamphorphosphinic acid, $\text{C}_{10}\text{H}_{14}\text{O} \cdot \text{CH} \cdot \text{PO}(\text{OH})_2$, was obtained by Bishop, Claisen, and Sinclair (Abstr., 1895, i, 63) as a bye-product in the preparation of hydroxymethylenecamphor, and was regarded by them as an acid phosphite; it crystallises with $\frac{1}{2}\text{H}_2\text{O}$, which is expelled at 110° ; its *ammonium*, *silver*, and *lead* salts are described. The *aniline* salt, $\text{C}_{10}\text{H}_{14}\text{O} \cdot \text{CH} \cdot \text{PO}(\text{OH}) \cdot \text{ONH}_3\text{Ph}$, melts at 195 – 196° . The *oxychlorophosphine*, $\text{C}_{10}\text{H}_{14}\text{O} \cdot \text{CH} \cdot \text{POCl}_2$, obtained by heating the acid (1 mol.) with phosphorus pentachloride (2 mols.), boils in a vacuum at 175 – 185° , and forms white, tabular crystals melting at 51° ; by the action of water, it is readily converted into the acid. The *anilide*, $\text{C}_{10}\text{H}_{14}\text{O} \cdot \text{CH} \cdot \text{PO}(\text{NHPh})_2$, crystallises in slender, yellow needles and melts at 227 – 228° ; the *p-toluidide* and the *p-diphenetide* melt at 210° and 137° respectively. The *diethyl* ester boils at 195 – 205° under 20 mm. pressure, and is decomposed by water. E. G.

Direct Introduction of Mercury into Aromatic Compounds. By OTTO DIMROTH and, in part, RICHARD METZGER and HERMANN ILZSÖFER (*Chem. Centr.*, 1901, i, 449–455; from *Habilschr.*, Tübingen, 1900).—Many of the results contained in this dissertation have been published already (Abstr., 1899, i, 54, 428), and the methods employed are those described before. The following observations appear to be new. The ease with which aromatic compounds form arylmercuric salts is on a level with the ease with which they can be nitrated or sulphonated; phenols and amines react readily, hydrocarbons and benzoic acid less readily, and nitrobenzene not at all. The mercury enters the usual position in the ring; in the case of benzoic acid, however, it enters the ortho-, and not the meta-position, but the reaction is otherwise abnormal, for a cyclic anhydride,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{Hg} \end{smallmatrix} \text{O}$, is formed. A solution of stannous chloride in alkali

hydroxides is found to reduce arylmercuric chlorides, HgRCl , to mercury and mercury aryls, HgR_2 . Alkalis do not decompose arylmercuric salts. Ammonium sulphide converts them into white sulphides; it does not attack mercury aryls; it instantly decomposes compounds in which the mercury is joined to nitrogen, such as mercurianiline, $\text{Hg}(\text{NHPh})_2$, black mercuric sulphide separating. *o*-Hydroxyphenylmercuric chloride unites with benzenediazonium chloride to form an azo-dye; under these circumstances, the para-isomeride is decomposed into mercuric chloride and hydroxyazobenzene, whilst the behaviour of hydroxyphenylenedimercuric chloride is of an intermediate character, some mercuric chloride being eliminated, and benzeneazo-*o*-hydroxyphenylmercuric chloride formed. Benzene-sulphonic acid forms a meta-mercury derivative, but this could not be obtained quite pure. Naphthalene also forms a mercury derivative.

The following substances appear to be described for the first time (the numbers given are melting points). From phenol: *o*-Mercuri-diphenol, $\text{Hg}(\text{C}_6\text{H}_4 \cdot \text{OH})_2$, from *o*-hydroxyphenylmercuric chloride and

sodium thiosulphate (compare Pesci, Abstr., 1899, i, 816). *Anisylmercuric iodides*, o, 168°, p, 227°. *o-Phenetylmercuric iodide*, 111°. *p-Hydroxyphenylmercuric oxide* decomposes at 180°. *Hydroxyphenylenedimercuric diacetate*, decomposes at 264—265°; invariably the product when mercuric acetate acts on phenol. *Benzeneazo-o-hydroxyphenylmercuric chloride*, red, 147°; crystallised with 1CMeO·OH, yellowish-brown, 126—128°; with $1\frac{1}{2}$ H₂O, yellow, about 125°; the last compound loses its water in a desiccator, forming a hygroscopic powder that takes up 1H₂O in the air, and at a higher temperature forms the substance melting at 147°. *Benzeneazo-p-hydroxyphenylmercuric chloride*, red, 130—131°; *acetate*, yellow. *Benzeneazo-o-hydroxyphenylmercuric acetate*, yellow, 197—198°. *Benzeneazohydroxyphenylenedimercuric dichloride*, about 165—170° (crystallised with 1CMeO·OH, brownish-red), is formed in small amount along with the preceding compound.

From *p*-cresol: *4-Hydroxy-1-methylphenylene-3:5-dimercuric acetate*, decomposes at about 200°. *4-Hydroxy-1-methylphenyl-3-mercuric chloride*, 166°; solid again at 183°; *benzoate*, 241—242°; *3-iodo-4-hydroxy-1-methylbenzene* (*o-iodocresol*), 37°, boils at 117° under a pressure of 12 mm. *Hydroxymethylphenylmercuric oxide* decomposes in light. *Benzeneazohydroxymethylphenylmercuric acetate*, red, 269°; *chloride*, yellowish-brown, decomposes about 249°; *benzeneazohydroxymethylbenzene* (*benzeneazo-p-cresol*), 108—109°.

From phenetole (compare Michaelis, Abstr., 1894, i, 191): *p-Phenetylmercuric acetate*, 234°. No *o*-isomeride discovered.

From aniline: *p-Aminophenylmercuric acetate*, 166—167° (compare Piccini and Ruspagliari, Abstr., 1893, i, 322), *acetyl derivative*, 220—221°; *chloride*. A second product, 158—160°, probably the isomeric *o*-acetate, was also obtained; *acetyl derivative*, 158—160°.

From dimethylaniline (compare Pesci, Abstr., 1894, i, 248): *p-Dimethylaminophenylmercuric acetate*, 165°; *chloride*, 225°.

From benzenesulphonic acid (see preceding page): By treating the product with bromine, *m-bromobenzenesulphonic acid* and some *dibromobenzenesulphonic acid* are obtained; the sodium salt of the former crystallises with 1H₂O.

From benzoic acid: *Mercuric benzoate*, 165°, when heated yields the amorphous *anhydride* of *o-carboxyphenylmercuric hydroxide* (*o-hydroxymercuric benzoic anhydride*; see preceding page).

From naphthalene: *α-Naphthylmercuric acetate*, 245—250°; *chloride*; *naphthylenedimercuric dichloride*. C. F. B.

Organic Magnesium Compounds of the Benzene Series. By TISSIER and GUIGNARD (*Compt. rend.*, 1901, 132, 1182—1184).—The haloid derivatives of benzene and its homologues react readily with magnesium in presence of ether, forming crystalline compounds of the type MgPhBr and C₇H₇·MgBr, analogous to those obtained with the paraffins. These compounds react energetically with acid chlorides and anhydrides, esters, and primary and secondary aldehydes, yielding products which will be described later.

Magnesium phenyl bromide with methyl benzoate yields triphenylcarbinol in almost theoretical quantity; with acetone, it yields dimethylphenylcarbinol, and with acetyl chloride, diphenylethylene, CPh₂:CH₂. C. H. B.

Organic Chemistry.

Composition of Texas Petroleum. By CHARLES F. MABERY (*J. Amer. Chem. Soc.*, 1901, 23, 264—267. Compare Abstr., 1900, i, 577).—A specimen of oil from the Lucas well in Jefferson Co. possessed a strong odour of hydrogen sulphide, had a sp. gr. 0·920 at 20°, and contained 2·16 per cent. of sulphur, and more than 1 per cent. of nitrogen. By fractional distillation under 14 mm. pressure and subsequent treatment with fuming sulphuric acid, the following hydrocarbons were isolated: fraction 130—135°, $C_{12}H_{22}$, sp. gr. 0·8553 at 20°; fraction 155—160°, $C_{14}H_{26}$, sp. gr. 0·8746, molecular refraction 62·36; fraction 190—195°, $C_{16}H_{30}$, sp. gr. 0·8915, molecular refraction 71·64; the residue left above 300° showed a sp. gr. 14° Beaumé.

The author suggests that these hydrocarbons possess the structure of a dihexahydrodiphenyl and its homologues. E. G.

Hexyl Bromide. By ANTOINE MOUNEYRAT (*Bull. Soc. Chim.*, 1901, [iii], 25, 543).—A reply to Bodroux (this vol., i, 306). N. L.

Oxidation of Primary Alcohols by Contact-action. By J. AUGUSTE TRILLAT (*Compt. rend.*, 1901, 132, 1227—1229).—On passing a mixture of air and the vapour of one of the primary alcohols of the fatty series over a platinum spiral heated to redness, the corresponding aldehyde is always formed, and represents from 1·8 to 1·5 per cent. of the alcohol used. The presence of water vapour does not modify the oxidation. Methyl and ethyl alcohol also yield methylal and acetal respectively. The latter action is reversible, as on passing the vapour of either of these acetals over a spiral, the aldehyde and alcohol are regenerated, a decomposition accompanied by a sufficient development of heat to render the spiral incandescent. Even in the absence of air, acetaldehyde is formed from ethyl alcohol. In the presence of platinum black or porous substances, the alcohols are oxidised to the corresponding acids. Besides the alcohols mentioned, the author has experimented with propyl, isopropyl, normal butyl, isoamyl, normal heptyl, and primary octyl alcohols. K. J. P. O.

Alcohols and Calcium Carbide. By PIERRE LEFEBVRE (*Compt. rend.*, 1901, 132, 1221—1223. Compare Abstr., 1900, i, 323).—On passing amyl, isobutyl, ethyl and methyl alcohols over calcium carbide heated at about 500° in tubes of iron or of Jena glass, a mixture of gases is obtained, which, in all four cases, consists chiefly (from 60—70 per cent.) of hydrogen. When a glass tube is used, amyl alcohol yields, besides hydrogen, acetylene 2·5, ethylene 4·9, carbon monoxide 8·6, carbon dioxide 2·2, ethylene hydrocarbons 8·6, and ethane 8·0 per cent. In an iron tube, the ethane increases at the expense of the ethylene hydrocarbons. When the calcium carbide is replaced by porcelain, only a trace of acetylene is formed, and the carbon monoxide increases to 12·4 and the ethylene hydrocarbons to 14·3 per cent., whilst 4·2 per cent. of ethane is produced. Analyses of the bromine derivatives of

the ethylene hydrocarbons show that they consist of propylene ($\frac{1}{2}$ to $\frac{3}{4}$), a trace of butylene, and the remainder β -methyl- β -butylene; no trimethylene is present.

From *isobutyl* alcohol were produced, acetylene 3.8, ethylene 4.8, carbon monoxide 6.8, *isobutylene* 7.8, ethane 13.4, and carbon dioxide 1.9 per cent. From ethyl alcohol were obtained, acetylene 3.6, ethylene 9.1, carbon monoxide 4.5, ethylene hydrocarbons 0.31, ethane 9.6, and carbon dioxide 4.4 per cent.; from methyl alcohol, acetylene 1.4, ethylene 4.2, carbon monoxide 8.3, ethylene hydrocarbons 2.5, ethane 13.8, and carbon dioxide 1.3 per cent. The liquid products of the reaction consisted in all cases (with the exception of methyl alcohol) of the aldehyde corresponding with the alcohol, and amounted to about 10 per cent. of the alcohol used.

K. J. P. O.

Molecular Compound of Methyl Iodide with Methyl Alcohol. By JEAN MEUNIER (*Bull. Soc. Chim.*, 1901, [iii], 25, 572—573).—If the product of the interaction of methyl alcohol, iodine, and phosphorus produced in the preparation of methyl iodide is distilled without removal of the methyl alcohol by washing with water, the compound $\text{MeI}, \frac{1}{3}\text{CH}_3\text{O}$ is obtained. This is a colourless, highly refractive liquid which boils at 37.9° , and has a sp. gr. 2.0807 at 15° ; it is readily decomposed by water.

N. L.

Active Amyl Derivatives. By PHILIPPE A. GUYE (*Bull. Soc. Chim.*, 1901, [iii], 25, 544—551. Compare Abstr., 1895, i, 202, 317, and ii, 472; 1897, ii, 238; 1898, ii, 469; 1899, ii, 718; 1900, ii, 253).—The amyl derivatives, the optical properties of which have been previously studied by the author, were prepared from Claudon's amyl alcohol, having a rotatory power $[\alpha]_D -4.52$ at 20° , whereas pure active amyl alcohol, according to Marckwald and Mackenzie (this vol., i, 248), has $[\alpha]_D -5.90$ at 20° . A number of observations bearing on the subject are now recalled from the author's researches, and it is shown that the *relative* values previously found for the rotatory powers of amyl derivatives are probably correct, and may be converted into the approximate *absolute* values by multiplying by the factor $5.90/4.52$ or 1.305. Tables of the original and corrected values for a number of compounds are given in the paper.

N. L.

Action of Aluminium Chloride on Aliphatic Alcohols. By GUSTAVE PERRIER and ISIDORE POUGET (*Bull. Soc. Chim.*, 1901, [iii], 25, 551—556).—The action of aluminium chloride on aliphatic alcohols in the cold results in the formation of additive compounds, whilst if the alcohol is heated with a large excess of aluminium chloride, substitution derivatives are formed. The following *compounds*, all of which are white, crystalline substances decomposed by water, have been prepared from methyl, ethyl, and *isobutyl* alcohols: $\text{Al}_2\text{Cl}_6, 10\text{MeOH}$; $\text{Al}_2\text{Cl}_4(\text{OMe})_2$; $\text{Al}_2\text{Cl}_6, 8\text{EtOH}$; $\text{Al}_2\text{Cl}_3(\text{OEt})_3$; $\text{Al}_2\text{Cl}_6, 4\text{C}_4\text{H}_9\cdot\text{OH}$; $\text{Al}_2\text{Cl}_4(\text{OC}_4\text{H}_9)_2$. Similar compounds are also formed from *n* propyl and *isoamyl* alcohols.

N. L.

Condensation of the true Acetylene Hydrocarbons with Formaldehyde. Synthesis of Primary Alcohols of the Acetylene Series. By CHARLES MOUREU and H. DESMOTS (*Compt. rend.*, 1901, 132, 1223—1226).—On treating the sodium derivatives

of acetylene hydrocarbons suspended in absolute ether with excess of trioxymethylene, a reaction immediately takes place. After removing the sodium with dilute sulphuric acid and evaporating the ether, the alcohol formed is fractionated under reduced pressure; the yield is about 30 per cent. From *c*-nanthylidene [heptinene] *amylpropargyl* [*β*-octinyl] alcohol, $\text{CH}_2\text{Me} \cdot [\text{CH}_2]_3 \cdot \text{C} \equiv \text{C} \cdot \text{CH}_2 \cdot \text{OH}$, is obtained as a colourless oil boiling at 98° under 13 mm. pressure, and having a sp. gr. 0.8933 at 0° . The *acetate* boils at 113 – 114° under 16 mm. pressure. In the same reaction is also formed a compound, $\text{C}_{16}\text{H}_{26}\text{O}$, which is possibly a condensation product of 2 mols. of *β*-octinyl alcohol. It boils at 178° under 16 mm. pressure, has the sp. gr. 0.907 at 0° and 0.892 at 19° , and gives n_D 1.474 at 19° .

Phenylacetylene yields *phenylpropargyl alcohol*, $\text{CPh} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{OH}$, which is a colourless oil boiling at 139° under 16 mm. pressure and having a sp. gr. 1.0811 at 0° . The *acetate* boils at 146° under 16 mm. pressure. Neither of these alcohols solidifies at -23° ; each forms a crystalline compound with aqueous solutions of mercuric chloride, reduces ammoniacal silver nitrate, and is not affected by boiling with potassium hydroxide solution. As the typical hydrogen atom of the acetylene hydrocarbons has disappeared, compounds with silver, &c., are not obtainable.

K. J. P. O.

Chloro- and Bromo-methyl Alcohols. By FRANZ M. LITTERSCHEID (*Annalen*, 1901, 316, 157–195).—A commercial “chloromethyl alcohol” was found to consist principally of chloromethyl ether mixed with small quantities of *s*-dichloromethyl ether and dichlorotrioxytetramethylene, $\text{O}(\text{CH}_2 \cdot \text{O} \cdot \text{CH}_2\text{Cl})_2$, together with traces of methylal and varying amounts of hydrogen chloride. Chloromethyl ether was identified by its boiling point and the analysis of the double salts of its compounds with trimethylamine and pyridine, the following compounds being described: $(\text{OMe} \cdot \text{CH}_2 \cdot \text{NMe}_3\text{Cl})_2\text{PtCl}_4$,

$(\text{OMe} \cdot \text{CH}_2 \cdot \text{NMe}_3\text{Cl})_2\text{AuCl}_3$,
 $(\text{OMe} \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_5\text{Cl})_2\text{PtCl}_4$, and $(\text{OMe} \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_5\text{Cl})\text{AuCl}_3$ (compare Hemmelmayr, *Abstr.*, 1892, 504).

s-Dichloromethyl ether was identified in a similar manner, the following double salts being described: $\text{O}(\text{CH}_2 \cdot \text{NMe}_3\text{Cl})_2\text{AuCl}_3$ and $[\text{O}(\text{CH}_2 \cdot \text{NMe}_3\text{Cl})_2]_2\text{PtCl}_4 \cdot \text{H}_2\text{O}$, the latter melting at 237° .

Dichlorotrioxytetramethylene yields the amorphous double salt, $\text{O}(\text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{NMe}_3\text{Cl})_2\text{PtCl}_4 \cdot \text{H}_2\text{O}$, and the corresponding aurichloride crystallising with $1\text{H}_2\text{O}$.

When hydrogen chloride reacts with gaseous formaldehyde, the chief products are *s*-dichloromethyl ether and dichlorotrioxytetramethylene (compare Grassi and Maselli, *Abstr.*, 1899, i, 409).

The chief product of the action of hydrogen bromide on trioxymethylene, or on an aqueous solution of pure formaldehyde, is *s*-dibromomethyl ether; no evidence could be obtained that bromomethyl alcohol is formed under these conditions (compare Henry, *Bull. Acad. Roy. Belg.*, 1893, [iii], 26, 615).

With trimethylamine, the bromo-ether yields the bromide, $\text{O}(\text{CH}_2 \cdot \text{NMe}_3\text{Br})_2 \cdot \text{H}_2\text{O}$; this salt loses water when dried at 100° , and melts at 205° .

G. T. M

Compounds of Methyl Sulphide with Haloids of Metals. By FRANCIS C. PHILLIPS (*J. Amer. Chem. Soc.*, 1901, 23, 250—258).—When methyl sulphide is added to a solution of palladium dichloride, the compound $\text{PdCl}_2 \cdot 2\text{Me}_2\text{S}$ is produced as a voluminous, yellow, micro-crystalline precipitate, which dissolves readily in boiling water and separates in orange needles on cooling. In solution, it is reduced by carbon monoxide, or more slowly by hydrogen, whilst in the solid state it is reduced by hydrogen in the cold with liberation of methyl sulphide and hydrogen chloride. Its solubility in water is 0.15 per cent. at 26.1° ; it dissolves in most organic solvents, melts at 124° , and, when heated more strongly, decomposes with formation of methyl sulphide, methyl chloride, and palladium sulphide.

Methyl sulphide combines with mercuric chloride to form a white, crystalline compound, $3\text{HgCl}_2 \cdot 2\text{Me}_2\text{S}$, which is slightly soluble in water and more so in alcohol; when heated rapidly, it melts at about 150 — 151° with evolution of methyl sulphide, but if heated more slowly, it decomposes and melts at a much higher temperature. This substance was first obtained by Loir (*Annalen*, 1853, 87, 369), who assigned to it the formula $\text{HgCl}_2 \cdot \text{Me}_2\text{S}$.

If methyl sulphide is added to a concentrated solution of cupric chloride, a white, crystalline substance, $\text{CuCl}_2 \cdot \text{Me}_2\text{S}$, slowly separates, which, when heated in nitrogen, evolves methyl sulphide, and leaves finally a residue of copper sulphide and copper; it is almost insoluble in water and the usual organic solvents.

Methyl sulphide reacts with a solution of auric chloride with formation of a compound, $\text{AuCl}_3 \cdot \text{Me}_2\text{S}$, which separates as a white, flocculent precipitate, but if left in the dark with a slight excess of methyl sulphide forms crystalline needles; it is rapidly decomposed by sunlight, yielding gold, methyl sulphide, and hydrogen chloride; when it is heated in nitrogen, methyl sulphide is evolved and metallic gold is left as a residue. E. G.

Constitutional Formulæ of Acids. By DANIEL VORLÄNDER (*Ber.*, 1901, 34, 1632—1637).—It is pointed out that all pronounced organic (and most inorganic) acids possess the atomic grouping $\text{H} \cdot \overset{1}{\text{E}} \cdot \overset{2}{\text{E}} \cdot \overset{3}{\text{E}} \cdot \overset{4}{\text{E}}$ (for example, $\text{H} \cdot \overset{1}{\text{O}} \cdot \overset{2}{\text{C}} \cdot \overset{3}{\text{O}}$). The mobility of the hydrogen atom depends firstly on the non-metal, 2, and secondly on the unsaturated character of the linking between the non-metals, 3 and 4 (called by the author the “reactive group”).

The hydrogen is far less movable in the absence of an unsaturated linking so placed, as in the types $\text{H} \cdot \overset{1}{\text{E}} \cdot \overset{2}{\text{E}}$ and $\text{H} \cdot \overset{1}{\text{E}} \cdot \overset{2}{\text{E}} \cdot \overset{3}{\text{E}} \cdot \overset{4}{\text{E}}$. As examples, the properties of the hydrogen atom in the aldehyde group $\text{H} \cdot \overset{1}{\text{C}} \cdot \overset{2}{\text{O}}$, and in the acid group $\text{H} \cdot \overset{1}{\text{O}} \cdot \overset{2}{\text{C}} \cdot \overset{3}{\text{O}}$, are compared; and also in the groupings $\text{H} \cdot \overset{1}{\text{O}} \cdot \overset{2}{\text{C}} \cdot (\overset{3}{\text{C}} \cdot \overset{4}{\text{C}})_3$ in triphenylcarbinol, and $\text{H} \cdot \overset{1}{\text{O}} \cdot \overset{2}{\text{C}} \cdot \overset{3}{\text{C}}$ in phenol. The acid character of the hydroxymethylene derivatives similarly finds its explanation in the atomic grouping $\text{H} \cdot \overset{1}{\text{O}} \cdot \overset{2}{\text{C}} \cdot \overset{3}{\text{C}}$. This grouping is absent in hypochlorous acid, $\text{H} \cdot \overset{1}{\text{O}} \cdot \overset{2}{\text{Cl}}$, which is very feebly acidic, despite the presence of the non-metal chlorine, which gives to hydrochloric acid such powerful acid properties. K. J. P. O.

Ethyl Nitroacetate. By A. WAHL (*Compt. rend.*, 1901, 132, 1050—1053. Compare this vol., i, 4).—Ethyl nitromalonate, conveniently prepared by adding ethyl malonate to fuming nitric acid at 20—30° (compare Franchimont, *Abstr.*, 1889, 1143), is separated from the product of reaction in the form of its *potassium* derivative, $C_7H_{10}O_6NK$, a compound separating from alcohol in lemon-yellow crystals; the *sodium* derivative crystallises in pale yellow needles. These substances are both readily soluble in water, and when heated melt and deflagrate with extreme violence; they regenerate the ester on treatment with dilute acids.

Ethyl nitromalonate is a colourless liquid boiling unchanged at 127° under 10 mm. pressure; it has the sp. gr. 1.1988 at 20°, and 1.220 at 0°, and is slightly soluble in water, yielding a yellow solution. When heated with water under pressure at 160°, it is completely decomposed, hydrocyanic and oxalic acids being identified among the degradation products. On slowly adding an aqueous solution of potassium hydroxide to a boiling solution of the potassium derivative of ethyl nitromalonate, the latter is decomposed, and the product, after acidifying, gives a yellow oil; this on fractionation yields a colourless liquid boiling at 90—95° under 10 mm. pressure, which is identical with the ethyl nitroacetate obtained from ethyl dimethylacrylate. G. T. M.

Action of Acid Chlorides on Ethers in the presence of Zinc. By PAUL FREUNDLER (*Compt. rend.*, 1901, 132, 1226—1227. Compare this vol., i, 357).—The author draws attention to the fact that Descudé's results (*loc. cit.*) have been partly anticipated by Freund (*Annalen*, 1861, 118, 33), who found that by the action of zinc on a mixture of butyryl chloride and ethyl ether, ethyl butyrate, ethyl chloride, zinc chloride, and dipropyl diketone were formed. Using zinc chloride instead of zinc, Descudé obtained an ester and alkyl chloride. The author obtained the same result when employing a zinc-copper couple. K. J. P. O.

Waxes. By MAURITS GRESHOFF and J. SACK (*Rec. Trav. Chim.*, 1901, 20, 65—78).—A wax, $C_{37}H_{74}O_2$ (*cera musae*), found on the leaves of the wild Javan banana-tree or "pisang," may be purified by melting in boiling water, and after solidification forms hard, white, vitreous masses having a crystalline, powdery fracture; it melts at 79—81°, has a sp. gr. 0.963 to 0.970 at 15°, and is sparingly soluble in all solvents. At 15°, light petroleum dissolves 0.4, acetone 0.5, ether 0.7, chloroform 1.7, and carbon disulphide 1.8 parts per 100. On hydrolysis with alcoholic potash, it yields a crystalline *acid*, $C_{24}H_{48}O_2$, melting at 71°, and an *alcohol*, $C_{13}H_{28}O$, melting at 78°; the acid is perhaps identical with the fatty acid of the same composition melting at 72°, which is formed by the hydrolysis of Carnauba wax.

Another wax (*cera fici*) is obtained from the sap exuding from incisions in the cortex of the wild fig tree or "gondang" (*Ficus ceriflua*); it is chocolate coloured externally, and cream coloured within, is not friable, and melts at about 60° to an extraordinarily viscous mass which only slowly solidifies, and is then nearly white. The molten wax has a sp. gr. 1.015 at 15°; by successive crystallisations from alcohol, it yields principally a crystalline compound, $C_{30}H_{52}O_2$,

melting at 61° . On hydrolysing this, an alcohol, *ficocerylic alcohol*, $C_{17}H_{35}O$, which crystallises from alcohol and melts at 198° , is obtained, along with an acid, *ficoceroic acid*, $C_{13}H_{26}O_2$, which melts at 57° . Small quantities of ficocerylic alcohol are present in the free state in the original wax, but are removed when the latter is crystallised from alcohol.

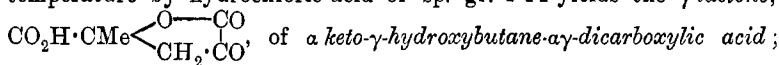
When the wax of the gondang is subjected to dry distillation, it yields acetic and propionic acids, a *hydrocarbon*, $C_{14}H_{26}$, which boils at 220° and has a sp. gr. 0.845 at 15° , and two crystalline *acids*, which can be separated by means of alcohol; one of these, $C_{44}H_{88}O$, melts at 51° and the other, $C_{12}H_{24}O_2$, at 54° .

The dry distillation of the wax of pisang yields a liquid *hydrocarbon*, $C_{16}H_{34}$, boiling at about 280° , and an *acid*, $C_{27}H_{54}O_2$, which crystallises from alcohol and melts at 58° .

Bees' wax when distilled yields an oil which boils evenly between 180° and 250° , the fractions of highest boiling point (220 — 250°) having the composition of a *hydrocarbon*, $C_{15}H_{30}$; a crystalline solid is also formed, which on hydrolysis yields an *acid*, $C_7H_{14}O_2$ (?), melting at 63° , and a non-saponifiable residue which is apparently a hydrocarbon of the series C_nH_{2n} , and melts at 56° .

W. A. D.

Action of Hydrochloric Acid on Pyruvic Acid. By A. W. K. DE JONG (*Rec. Trav. Chim.*, 1901, 20, 81—101).—The *sodium sulphite* compound, $CH_3 \cdot CO \cdot CO_2Na, NaHSO_3, H_2O$, of sodium pyruvate crystallises from water on slow evaporation in orthorhombic prisms [$a:b:c=0.7485:1:0.5258$], and when decomposed at the ordinary temperature by hydrochloric acid of sp. gr. 1.14 yields the γ -lactone,



of a *keto- γ -hydroxybutane- α - γ -dicarboxylic acid*; this can also be obtained by leaving pyruvic acid in contact with hydrochloric acid of sp. gr. 1.14 for several months, or more rapidly (after about 8 days) by passing dry hydrogen chloride through pyruvic acid until crystals begin to form. It is slowly formed by the spontaneous condensation of pyruvic acid (compare Wolff, *Abstr.*, 1899, i, 483), and is usually present in commercial samples of the latter; when pure, it crystallises in needles, melts at 115 — 116° and is hygroscopic. Its formula was confirmed by a molecular weight determination by the cryoscopic method in glacial acetic acid solution. The *barium* salt, with $1\frac{1}{2}H_2O$, of the lactone is obtained by neutralising it with barium carbonate, and adding alcohol. It forms slender needles, is easily soluble in water and, when boiled with it, is transformed into the *barium* salt, $[CO_2H \cdot CMe(OH) \cdot CH_2 \cdot CO \cdot CO_2]_2Ba$, of α -keto- γ -hydroxybutane- α - γ -dicarboxylic acid; this forms a crust of needles, is less soluble in water than the salt of the lactone, and when decomposed by dilute sulphuric acid yields, not the corresponding acid, but its lactone. The normal *barium* salt, $\begin{array}{c} CMe(OH) \cdot CO_2 \\ \diagdown CH_2 \diagup CO \end{array} > Ba, 1\frac{1}{2}H_2O$, formed by neutralising a warm solution of the lactone with barium carbonate, is amorphous and easily soluble in water.

The *phenylhydrazone*, $CO_2H \cdot CMe \begin{array}{c} \diagup O \diagdown CO \\ \diagdown CH_2 \diagup C:N \cdot NHPh \end{array}$, of the lactone

forms sheaves of slender, yellow needles, melts at 191—192°, and usually crystallises with 2H₂O, although from concentrated solutions it is obtained anhydrous. Tests are given which distinguish this phenylhydrazone from the phenylhydrazone of pyruvic acid which melts at 185° as stated by Japp and Klingemann (*Trans.*, 1887, 51, 533) and not at 192° as stated by E. Fischer (*Abstr.*, 1884, 1150); it is probable that Fischer's compound was the phenylhydrazone of the new lactone. The same phenylhydrazone is formed on adding phenylhydrazine hydrochloride to a solution of the barium salt of the lactone, but the two barium salts of the acid yield instead the *phenylhydrazone*, CO₂H·CMe(OH)·CH₂·C(CO₂H):N·NHPh, of this acid; it crystallises in needles with 2H₂O and melts at 154—155°.

α -Keto- γ -hydroxybutane- $\alpha\gamma$ -dicarboxylic acid, which can be considered as formed by the aldol condensation of pyruvic acid, when heated with hydrochloric acid yields pyrotartaric acid; with sodium hydroxide, it forms methylidihydrotrimesic acid.

W. A. D.

Action of Sodium on the Esters of Organic Acids. By SERGIUS N. REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 235—239).—The author discusses the mechanism of the formation of ethyl acetoacetate by the action of sodium on ethyl acetate, as given by Claisen, with whose views the results given in the following two papers agree.

T. H. P.

Synthesis of α -Methyl- β -ethylhydracrylic Acid. By A. ASTACHOFF and SERGIUS N. REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 239—241).—The ethyl ester of this acid, already described by Hantzsch and Wohlbrück (*Abstr.*, 1887, 717) is obtained by the action of zinc on a mixture of ethyl α -bromopropionate and propaldehyde and decomposition of the resulting product with water.

T. H. P.

Synthesis and Properties of α -isoPropyl- β -isobutylhydracrylic Acid. By D. PROTOPOPOFF and SERGIUS N. REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 242—246).—The constitution of α -iso-propyl- β -isobutylhydracrylic acid, C₁₀H₂₀O₃, obtained by Wohlbrück (*Abstr.*, 1887, 1099) by the action of sodium on ethyl isovalerate, is confirmed by its formation when zinc, ethyl bromoisovalerate, and isovaleraldehyde interact. The ethyl ester, C₁₂H₂₄O₃, forms a thick oil distilling at 188—190° under 140—150 mm. pressure. The sodium and basic barium, (C₁₀H₁₉O₃)₂Ba, Ba(OH)₂, salts were analysed. The mean value of the electrical conductivity constant is $K = 0.00199$, the mean number for secondary β -hydroxy-acids being 0.0018. By distillation with 10 per cent. sulphuric acid, the acid yields: (1) a lactone,

CHMe₂·CH< $\begin{matrix} \text{CH}_2\cdot\text{CHPr}^\beta \\ \text{O} \text{---} \text{CO} \end{matrix}$, which is a neutral, colourless, viscous

liquid with a smell resembling that of camphor; it does not decolorise bromine, is slightly soluble in water, and boils at 241—243°; (2) a small quantity of colourless crystals melting at 68—69.5° which have an acid reaction and decolorise bromine and represent probably an $\alpha\beta$ -unsaturated acid, since the original hydroxy-acid has a hydrogen atom in the α -position.

T. H. P.

Urano-oxalic Acid. By VOLKMAR KOHLSCHÜTTER and H. ROSSI (*Ber.*, 1901, 34, 1472—1479).—When oxalic acid is added to a solution of a uranyl salt reduced with copper or with hyposulphurous acid, a green, crystalline precipitate of insoluble uranous oxalate, $U(C_2O_4)_2 \cdot 6H_2O$ (Seekamp, *Annalen*, 1862, 122, 115), is produced; the precipitate is formed quantitatively and can be used for estimating uranium or for recovering uranium from complex residues; unlike other uranous salts, it is not readily oxidised; it is insoluble in water and in dilute acids, but dissolves in concentrated hydrochloric acid; alkalis convert it into uranous hydroxide. With ammonium and potassium oxalates, it gives dichroic solutions of urano-oxalates which are green in thick layers and red in thin layers; *potassium urano-oxalate*, $U(\cdot O \cdot CO \cdot CO_2K)_4$, forms rhombic crystals, which are only slightly coloured, but gives a dichroic solution; it is very stable when compared with other uranous salts; *barium urano-oxalate*, $U(C_2O_4)_4Ba_2 \cdot 9H_2O$, is a violet, crystalline compound. Urano-oxalic acid has not been isolated, but acid salts containing only a small amount of alkali are produced by the action of dilute hydrochloric acid on the urano-oxalates, the acid *ammonium salt*, formulated as $CO_2H \cdot CO_2 \cdot U(C_2O_4) \cdot C_2O_4 \cdot U(C_2O_4) \cdot CO_2 \cdot CO_2 \cdot NH_4 \cdot 8H_2O$, forms microscopic prisms, and is converted directly into uranous oxalate by loss of a molecule of water when the alkali is completely removed.

T. M. L.

Semialdehyde of β -Methyladipic Acid. By CARL D. HARRIES and OTTO SCHAUWECKER (*Ber.*, 1901, 34, 1498—1501).—Citronellal-dimethylacetal (Abstr., 1900, i, 331) is converted by oxidation with potassium permanganate into the *dimethyl semiacetal of β -methyladipic acid* (the dimethylacetal of 3-methylhexane-1-al-6-carboxylic acid), $CO_2H \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CH(OMe)_2$, which is a faintly yellow liquid and boils at 149—152° under 7—8 mm. pressure. When preserved for some time, or allowed to remain in solution in acidified water, it yields the *aldehydo-acid*, $CO_2H \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CHO$, which is a colourless, refractive liquid, boils at 153—155° under 12 mm. pressure, is readily soluble in water, alcohol, or ether, and has a sp. gr. 1.0959 at 10°. It reduces Fehling's solution on boiling, and reddens magenta-sulphurous acid. The *silver salt* is a white, microcrystalline powder; the *semicarbazone*, $NH_2 \cdot CO \cdot NH \cdot N \cdot CH \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CO_2H$, crystallises in white plates melting at 156—157°.

A. H.

Influence of Molybdates and Tungstates on the Specific Rotation of Tartrates. By HERRMANN ITZIG (*Ber.*, 1901, 34, 1372—1380).—It has been shown, in the case of tartaric acid (Abstr., 1900, i, 273), that a maximum value of the specific rotation is obtained when two alkali ions are present for every tartrate ion. This is also found to be the case with sodium hydrogen tartrate; the maximum value of $[\alpha]_D$ for $1C_4H_4O_6HNa$ is, with $\frac{1}{2}Na_2MoO_4$, $+2+221.3$; with $\frac{1}{6}(NH_4)_6Mo_7O_{24}$, $+456.7$; with $\frac{1}{2}Na_2WO_4$, $+133.6$; with $\frac{1}{10}Na_{10}W_{12}O_{41}$, $+220$. The rotation is also raised by yellow, soluble molybdic acid, a maximum value, $+320.6$, being obtained with $2MoO_3$.

As regards normal tartrates, the rotation of Rochelle salt is hardly affected by normal sodium molybdate, but it is raised largely by the salt $(NH_4)_6Mo_7O_{24}$, and to a less degree by $Na_{10}W_{12}O_{41}$, although in

neither of these cases does the maximum correspond with a simple molecular ratio; it is also raised by yellow, soluble molybdic acid, a maximum value, +521.8, being obtained with $1\text{C}_4\text{H}_4\text{O}_6\text{KNa} : 1\text{MoO}_3$. The salt, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, also raises the rotation of calcium tartrate in hydrochloric acid solution, and of tartar emetic; the rotation of the latter was depressed by normal sodium molybdate, but antimonious acid separated from the solution after a time.

Diacetyltartaric acid and glucose are not influenced, as regards their rotation, by molybdates or tungstates. C. F. B.

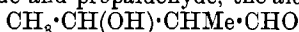
Oxidation of *l*-Arabonic Acid and *l*-Xylonic Acid. By OTTO RUFF (*Ber.*, 1901, 34, 1362—1372. Compare Abstr., 1900, i, 139).—[With ADOLF MEUSSER.]—*l*-Arabinose was obtained from cherry gum and converted into calcium *l*-arabonate by Kiliani's method (Abstr., 1887, 229). This salt was oxidised with hydrogen peroxide and ferric acetate to *l*-erythrose, the *phenylbenzylhydrazone* of which melts at 105° (corr.), and has specific rotation $[\alpha]_D + 32.8^\circ$ in 5 per cent. alcoholic solution at 20°. From this hydrazone, formaldehyde liberates (Abstr., 1900, i, 77) *l*-erythrose, a colourless syrup with initial and final specific rotations $[\alpha]_D + 2.40^\circ$ and $+ 21.5^\circ$ respectively, in 5 per cent. solution at 20° (compare Weil, Abstr., 1900, i, 140); the yellow *osazone* of this tetrose melts at 164° (corr.). Bromine oxidises the crude erythrose in aqueous solution to *l*-erythronic acid, the *brucine* salt of this acid melts at 212°, and has $[\alpha]_D - 30.7^\circ$ and $- 28.4^\circ$ at 20° in 9 and 4 per cent. solution respectively; the *lactone* melts at 104° (corr.) and has $[\alpha]_D 71.74^\circ$ in 2.8 per cent. aqueous solution at 20°; the *phenylhydrazide* melts at 127°. Starting from a mixture of calcium *d*- and *l*-arabonates, an attempt was made to prepare *r*- or *dl*-derivatives. In the case of the phenylbenzylhydrazone, no *r*-compound could be obtained; from the concentrated solution of the two optical isomerides either could be crystallised at will by inoculating the solution with a crystal of the desired isomeride. The *osazone* obtained melted at the same temperature as the supposed *l*-erythrosazone, and a mixture of the two substances had still the same melting point, so that racemisation had probably taken place in the preparation of the *osazone* from the active erythrose. The yield of erythrose obtained by the method described is but small.

[With HUGO KOHN.]—Still smaller is the yield of tetrose obtained with *l*-xylose as a starting-point (prepared from wheat straw by Schulze and Tollens' method, Abstr., 1892, 1420). This was oxidised in aqueous solution with bromine to *l*-xylonic acid, the calcium salt of which was then oxidised with hydrogen peroxide and ferric acetate to *l*-threose. The *phenylbenzylhydrazone* of this tetrose melts at 194.5° (corr.); the *osazone* is identical with that obtained from *d*-erythrose (Abstr., 1900, i, 139); the sugar itself is reduced by sodium amalgam to *l*-erythritol (Maquenne, Abstr., 1900, i, 424), which was isolated in the form of its benzoic acetal, melting at 204—205°. C. F. B.

Condensation of Aldehydes. By ADOLF LIEBEN (*Monatsh.*, 1901, 22, 289—313).—A summary of the work which has been carried out in the author's laboratory on this subject.

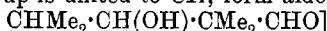
The first product of the condensation of 2 mols. of the same

aldehyde, or of different aldehydes, is always an aldol in which the hydroxyl is in the β -position to the CHO group; the condensation takes place between the aldehyde group of one mol. and the α -carbon atom of the other. In the condensation of two aldehydes, both of which possess hydrogen atoms united to the α -carbon atom, it is generally found that the CHO group more readily condenses with a CH group than with a CH_2 group, and with the latter more readily than with a CH_3 group; thus from acetaldehyde and propaldehyde, the aldol



is obtained.

The aldols which possess a hydrogen atom attached to the α -carbon atom, may be converted into unsaturated aldehydes with elimination of water. Such aldols must be derived from an aldehyde, in which the CHO group is linked to CH_3 or CH_2 . These are called by the author aldehydes of the first class. The second class of aldehydes, in which the CHO group is united to CH, form aldols [for example,



which cannot be converted into unsaturated aldehydes, as there is no hydrogen now attached to the α -carbon atom. In the third class of aldehydes, the CHO group is not linked to a carbon atom which is directly united to any hydrogen atoms; such aldehydes are formaldehyde, isobutyraldol, and benzaldehyde. They do not yield an aldol, but give Cannizzaro's reaction with alkaline condensing agents. Thus formaldehyde yields formic acid and methyl alcohol. The reaction is quantitatively represented by the equation $2\text{CH}_2\text{O} + \text{KOH} = \text{HCO}_2\text{K} + \text{CH}_3\cdot\text{OH}$, and is nearly complete after 11 days at a temperature of about 10° . Acetaldehyde and propaldehyde under similar conditions are converted chiefly into resins, only some 5 per cent. being transformed into acids. The author expresses the opinion that all aldehydes are capable of undergoing Cannizzaro's reaction, but that this reaction takes place so much more slowly than the aldol condensation that the former is practically entirely concealed.

The abnormal behaviour of isobutaldehyde in yielding octoglycol isobutyrate (Abstr., 1898, i, 353) or octoglycol and isobutyric acid is considered. The paper contains a list of the aldols so far prepared.

K. J. P. O.

New Reaction of Aldehydes. By ENRICO RIMINI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 355—362).—The formation of the hydroxamic acids may be used as a means of detecting and identifying aldehydes. These acids, which are readily recognisable by the intense reddish-violet coloration which their solutions give with ferric chloride, may be formed by the action on the aldehydes of nitrohydroxylaminic acid, but in this case a nitrite is also produced, and the latter often changes the reactions of the hydroxamic acids. For the preparation of the latter, it is therefore better to employ benzenesulphohydroxamic acid, which in presence of an aldehyde splits up according to the equation $\text{Ph}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{OH} = \text{Ph}\cdot\text{SO}_2\text{H} + \text{NOH}$, the oximido-residue combining with the aldehyde giving the corresponding hydroxamic acid. The reaction has been found to give positive results with a number of aldehydes, including formaldehyde, acetaldehyde,

valeraldehyde, acraldehyde, citral, glyoxal, glyceraldehyde, benzaldehyde, piperonaldehyde, anisaldehyde, salicylaldehyde, furfuraldehyde, δ -aminovaleraldehyde, and formic acid. The aldehyde is dissolved in alcohol, a few c.c. of a 2*N* potassium hydroxide added, then the calculated quantity of the benzenesulphohydroxamic acid, and finally a few more c.c. of the potassium hydroxide solution. The liquid is left for a short time, after which the alcohol is distilled off. The hydroxamic acids can readily be separated from the solution in the form of their copper salts, which are insoluble blue or green precipitates.

Copper piperonalhydroxamate, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_8 \cdot \text{C} \begin{smallmatrix} \text{NO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{Cu}$, is obtained as a pale green precipitate.

The *copper* salts of formalhydroxamic acid, $\text{CH} \begin{smallmatrix} \text{NO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{Cu} + \text{H}_2\text{O}$, acetalhydroxamic acid, $\text{CMe} \begin{smallmatrix} \text{NO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{Cu}$, and *isovaleralhydroxamic acid*, $\text{C}_4\text{H}_9 \cdot \text{C} \begin{smallmatrix} \text{NO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{Cu}$, were analysed.

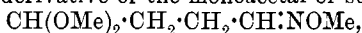
T. H. P.

Succindialdehyde. By CARL D. HARRIES (*Ber.*, 1901, 34, 1488—1498).—*Succindialdehyde*, $\text{CHO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO}$, can readily be prepared by passing nitrous fumes through succindialdoxime suspended in water, the neutralised liquid is then evaporated in a vacuum, and the residue distilled in vacuum. The dialdehyde is a hard, glassy mass of sp. gr. 1.23 at 19°, which becomes viscid at 25° and readily mobile at 70°, and boils at 65—66° under 11 mm. and at 160—170° under atmospheric pressure without decomposition. On standing in the air, it becomes yellow and viscid. It is sparingly soluble in water, ether, or benzene, readily so in hot alcohol; the vapour has a penetrating odour and an irritating effect on the skin and mucous membrane. It reduces alkaline Fehling's solution strongly in the cold, and produces a blue coloration with magenta and sulphurous acid. The aldehyde appears to exist in two forms, one of which is readily soluble in water and is perhaps the hydrate, whilst the solid form described above is anhydrous and sparingly soluble. The *monohydrate* is a thick liquid and boils at about 55° under 12 mm. pressure. The aldehyde is stable towards dilute acids, but becomes dark coloured and resinous with concentrated acids. It is, however, at once converted by alkalis into a yellow, amorphous mass, and reacts explosively with concentrated aqueous potash. It is converted by heating with water at 180° into furfuran, by boiling with ammonia and acetic acid into pyrrole, and by heating with phosphorus trisulphide into thiophen.

Succintetramethylacetal, $\text{C}_2\text{H}_4[\text{CH}(\text{OMe})_2]_2$, obtained by acting on the aldehyde with formimino-ether hydrochloride, has a sp. gr. 0.9897 at 19°, and boils at 201—202° under 772 mm. pressure. Dilute hydrochloric acid in the cold converts it into the dialdehyde. The *hydrogen sulphite*, $\text{C}_2\text{H}_4[\text{CH}(\text{OH}) \cdot \text{SO}_3\text{Na}]_2$, crystallises in slender needles. The diphenylhydrazone, which was previously obtained by Ciamician and Zanetti from the dioxime (*Abstr.*, 1890, 1120) is readily prepared by the direct action of phenylhydrazine acetate. The *monobromophenylhydrazone*, $\text{CHO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Br}$, crystallises in greenish

plates melting at 135—136°. The *dibromophenylhydrazone*, $C_2H_4(CH:N_2H \cdot C_6H_4Br)_2$, forms square, yellow crystals melting at 140—145° and is very unstable. The aldehyde condenses with *o*-phenylenediamine, forming a compound which melts at 175—177°, the nature of which has not yet been determined.

When succindialdoxime is treated with a solution of hydrogen chloride in methyl alcohol, it yields a small amount of succintetramethylacetal, together with a larger amount of *succinmonoaldehydoacetal imino-ether*, $CH(OMe)_2 \cdot CH_2 \cdot CH_2 \cdot C(OMe) : NH$, which boils at 82—83° under 20—21 mm. pressure, and has basic properties. *Dibenzoylsuccindialdoxime*, $C_2H_4(CH:N \cdot OBz)_2$, crystallises in indistinct plates melting at 152°. *Dimethoxysuccindialdoxime* is obtained by the action of sodium methoxide and methyl iodide, in the form of a brown oil, which with hydrogen chloride and methyl alcohol yields the *mono-oxime methyl ether* derivative of the monoacetal of succinic acid,



which boils at 180—200°. On treatment with hydrochloric acid, this is converted into the corresponding *derivative* of the aldehyde, $CHO \cdot CH_2 \cdot CH_2 \cdot CH : N \cdot OMe$, which boils at 67° under 10 mm. pressure.

A. H.

Symmetrical α -Diketones of the Aliphatic Series. By GIACOMO PONZIO (*J. pr. Chem.*, 1901, [ii], 63, 364—369. Compare Abstr., 1897, i, 317; 1899, i, 111, and 1900, i, 588).—By the action of concentrated nitric acid on ketone alcohols of the type $R \cdot CO \cdot CH(OH) \cdot R$, a number of fatty α -diketones are prepared. They are all yellow liquids, lighter than water, which distil without decomposing, forming a yellow vapour, and readily distil in steam.

Diethyl diketone (dipropionyl) (Abstr., 1897, i, 317) was isolated from the product of the action of nitric acid on dipropionin by distillation in steam, and then converted into the *oxime*, $C_2Et_2(N \cdot OH)_2$, which crystallises from benzene in white needles melting at 185°.

Dipropyl diketone (dibutyryl) was obtained together with *dinitropropane*, which dissolves in aqueous potassium carbonate, forming a yellow solution. The *potassium* salt, $C_2H_5O_4N_2K$, of the latter crystallises in yellow plates. *Dipropyl diketoxime*, $C_2Pr^a_2(NOH)_2$, forms white needles, melting at 175°. *Diisopropyl diketoxime*, $C_2Pr^i_2(NOH)_2$, prepared in an analogous manner to the oximes previously mentioned, forms white needles which melt at 163—164°. *Diisobutyl diketoxime*, $(CH_2Pr^b)_2 \cdot C_2(NOH)_2$, crystallises in silky, lustrous needles which melt at 195°.

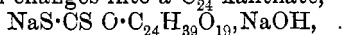
K. J. P. O.

Synthetic Action of Yeast Maltase. By ARTHUR CROFT HILL (*Ber.*, 1901, 34, 1380—1384).—The author disputes Emmerling's conclusions (this vol., i, 258) that, in the (reversed) hydrolysis of dextrose (*Trans.*, 1898, 73, 634), (1) the sugar formed is not fermentable; (2) the osazone isolated was *isomaltosazone*.

C. F. B.

Cellulose Xanthates. By CHARLES F. CROSS and EDWARD J. BEVAN (*Ber.*, 1901, 34, 1513—1520).—This is a general review of experimental results which the authors intend publishing later in detail. To form

the cellulose xanthates, the best proportion of the ingredients to use is that given by $C_6H_{10}O_5 : 2NaOH : CS_2$; the xanthate is derived from a hydrate, such as $C_6H_{10}O_6, H_2O$, the second mol. of sodium hydroxide becoming attached to the cellulose complex to form a compound of the type $NaS \cdot CS \cdot O \cdot C_6H_9O_4 \cdot NaOH$. In the xanthate initially formed, the cellulose is present as a C_6 complex, and the product is not precipitated by neutral dehydrating agents even after acidification; after 24 hours a C_{12} complex is formed, this being the principal ingredient of the so-called "viscose" solution. It is stable for some days, but at the period of coagulation changes into a C_{24} xanthate,



which is insoluble in water, soluble in dilute alkalis, and is precipitated from its original solution on adding acid.

For the methods of purification and analysis used, the original should be consulted; the percentage of alkali (NaOH), sulphur, and sodium was determined in the various cases. In determining the alkali, advantage was taken of the fact that it is not removed from combination with the $\cdot CS \cdot S$ group of the xanthate by dilute acetic acid, although dilute sulphuric acid effects complete decomposition. As a check on this method of determining the combined alkali, that based on the equation $2NaS \cdot CS \cdot OR + I_2 = (OR \cdot CS \cdot S)_2 + 2NaI$, using a normal solution of iodine, was employed, concordant results being obtained by the two methods.

W. A. D.

Oxycellulose and Hydrocellulose. By J. J. MURUMOW, J. SACK, and BERNHARD TOLLENS (*Ber.*, 1901, **34**, 1427—1434).—The oxycellulose obtained by the action of potassium chlorate and hydrochloric acid on cotton wool, when boiled with lime and water, yields cellulose, isosaccharinic acid, and dihydroxybutyric acid. In this respect, it resembles the oxycelluloses prepared from pine wood and nitric acid, from cotton wool, bromine, and calcium carbonate, and from cotton wool and nitric acid (see von Faber and Tollens, *Abstr.*, 1899, i, 854). Products very similar to, and possibly identical with, those yielded by the oxycelluloses are obtained when the hydrocellulose prepared by digesting cotton wool with sulphuric acid of sp. gr. 1.52—1.54 is boiled with lime and water.

T. H. P.

Cellulose, Oxycellulose, Hydrocellulose, the Pectins, and Tragacanth. By BERNHARD TOLLENS (*Ber.*, 1901, **34**, 1434—1441).—The author divides these compounds into the following classes: (1) celluloses; (2) hydrated celluloses, that is, hydrocelluloses and hemi-celluloses, which are non-reducing; (3) celluloses containing carboxyl groups, as, for example, the pectic acids; (4) celluloses with carboxyl and reducing (carbonyl) groups, to which belong the oxycelluloses and celloxin.

The properties and relations of these various classes of compounds are discussed. The author considers that the formula of hydracellulose (Bumcke and Wolfenstein, *Abstr.*, 1899, i, 852) is not ascertained with sufficient certainty to allow of any conclusions concerning other oxycelluloses being drawn, and he continues to regard the oxycelluloses as real oxidation products of cellulose.

Contrary to the views of Hilger and Dreyfus (*Abstr.*, 1900, i, 379)

the author holds that oxybassorin and also tragacanth contain carboxyl groups. From the products of hydrolysis of a sample of vermicelli tragacanth, the first-named authors (*loc. cit.*) obtained by crystallisation only arabinose; this sugar was previously obtained in this way by Widtsoe and Tollens (Abstr., 1900, i, 207), who also isolated fucose by precipitation as phenylhydrazone and decomposition of the latter by benzaldehyde.

T. H. P.

[Properties and Composition of Glycogen.] By JOSEPH NERKING (*Pflüger's Archiv*, 1901, 85, 313—319, 320—329).—See this vol., ii, 462.

Oxidation of Compounds containing Nitrogen. By DANIEL VORLÄNDER (*Ber.*, 1901, 34, 1637—1642. Compare this vol., i, 444).—The ready oxidation of various organic substances containing nitrogen is shown to depend on (1) the unsaturated character of tervalent nitrogen, and (2) on the presence of a hydrogen atom in position 3 (*loc. cit.*). Neither of these conditions alone suffices. Thus, ammonia and azobenzene both contain tervalent nitrogen, but no hydrogen atom in position 3, and cannot be oxidised easily. On the other hand, alkyl (aliphyl) amines, hydroxylamine, and hydrazine, in which such a hydrogen atom is present, are easily oxidised. In α -ethylhydroxylamine, this hydrogen atom is replaced, and consequently this substance is stable to Fehling's solution, whilst β -ethylhydroxylamine is readily oxidised. In salts of nitrogen bases, the nitrogen is saturated, and the compounds again become stable to oxidising agents.

Anilindiacetic acid, $N^{10}Ph(CH_2 \cdot CO_2H)_2$, and phenylglutaric acid, $CHPh(CH_2 \cdot CO_2H)_2$, are contrasted. The former, with the hydrogen atom in position 3 to the unsaturated nitrogen atom, is immediately oxidised by potassium permanganate, and gives a colour reaction with ferric chloride, whilst the latter with a saturated carbon atom is stable under these conditions.

K. J. P. O.

A new Glycine Anhydride. By LUIGI BALBIANO (*Ber.*, 1901, 34, 1501—1504. Compare Abstr., 1900, i, 632).—The examination of the compound $C_{22}H_{34}O_{13}N_{10}$, which was previously described, shows that it is in reality an anhydride of glycine, has the formula C_2H_3ON , and is completely converted into glycine by hydrolysis. It appears, however, to differ from the anhydride already described by Curtius and Goebel (Abstr., 1888, 576) which, however, is present in the washings obtained from the crude compound.

Small amounts of glycollic acid can be estimated in presence of glycine by evaporating with hydrochloric acid and extracting the dry mass with a mixture of alcohol and ether (1 of alcohol to 10 of ether) which dissolves the glycollic acid.

A. H.

Action of Hydrofluosilicic Acid on Potassium Ferricyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, 25, 327—328. Compare this vol., i, 262).—Solutions of hydrofluosilicic acid and of potassium ferricyanide react with one another, even in the absence of air, yielding a precipitate of Berlin blue, probably formed according to the equation $14K_3FeC_6N_6 + 21H_2SiF_6 + 3H_2O = 21K_2SiF_6 + 2Fe_4(FeC_6N_6)_3$

+ 48HCN + 3O. The reaction is not so delicate as with the ferrocyanide.
J. J. S.

Influence of Sunlight on Aqueous Solutions of Potassium Ferricyanide. By J. MATUSCHER (*Chem. Zeit.*, 1901, 25, 411—412).—Dilute aqueous solutions of potassium ferricyanide are decomposed by sunlight even in the absence of air, ferric hydroxide being precipitated. When the concentrations increase in the form of an arithmetical series, it is found that the amounts of precipitate form a decreasing arithmetical series.
J. J. S.

Ferricyanides of the Alkali Earths. By TH. FISCHER and P. MÜLLER (*Chem. Zeit.*, 1901, 25, 321—322).—Crystals of barium ferricyanide, $\text{Ba}_3\text{Fe}_2\text{C}_{12}\text{N}_{12} \cdot 20\text{H}_2\text{O}$, were prepared by neutralising the corresponding acid with barium carbonate and evaporating the solution to crystallisation. The *strontium* salt, $\text{Sr}_3\text{Fe}_2\text{C}_{12}\text{N}_{12} \cdot 14\text{H}_2\text{O}$, forms well-developed, reddish-brown prisms. The *calcium* salt crystallises with $12\text{H}_2\text{O}$ in small, glistening needles, and its aqueous solution is decomposed when warmed. The *magnesium* salt forms reddish-black, nodular masses, and when dried over sulphuric acid contains $10\text{H}_2\text{O}$; its aqueous solution is decomposed when heated. The following salts have also been prepared:— $\text{BaKFeC}_6\text{N}_6 \cdot 4\text{H}_2\text{O}$, hexagonal prisms; $\text{SrKFeC}_6\text{N}_6 \cdot 3\text{H}_2\text{O}$, deep ruby red prisms; $\text{CaKFeC}_6\text{N}_6 \cdot 3\text{H}_2\text{O}$, deep red plates much more stable than the simple calcium salt;

$\text{MgKFeC}_6\text{N}_6 \cdot 4\text{H}_2\text{O}$,
nodular masses; $\text{BaNaFeC}_6\text{N}_6 \cdot 3\text{H}_2\text{O}$, brownish-red lamellæ;
 $\text{SrNaFeC}_6\text{N}_6 \cdot 3\text{H}_2\text{O}$; $\text{CaNaFeC}_6\text{N}_6 \cdot 5\text{H}_2\text{O}$; $\text{MgNaFeC}_6\text{N}_6 \cdot 6\text{H}_2\text{O}$;
 $\text{BaNH}_4\text{FeC}_6\text{N}_6 \cdot 4\text{H}_2\text{O}$; $\text{SrNH}_4\text{FeC}_6\text{N}_6 \cdot 3\text{H}_2\text{O}$; $\text{CaNH}_4\text{FeC}_6\text{N}_6 \cdot 3\text{H}_2\text{O}$;
 $\text{MgNH}_4\text{FeC}_6\text{N}_6 \cdot 6\text{H}_2\text{O}$.
J. J. S.

Double Thiocyanates and the Ferric Thiocyanate Reaction. By ARTHUR ROSENHEIM and ROBERT COHN (*Zeit. anorg. Chem.*, 1901, 27, 280—303).—Three series of mercury double thiocyanates are known. The *monothiocyanates*, HgSCNCl , HgSCNBr , and $\text{HgSCN} \cdot \text{OAc}$, are described. Direct physical evidence of the presence of the complex cation, HgSCN , in these salts cannot be obtained on account of their slight solubility. When, however, they are treated with a solution of alkali chromate or dichromate, bright yellow precipitates are obtained which contain the thiocyanate radicle chemically combined, and the authors consider this to be evidence of the presence of the cation HgSCN in these salts.

The *mercury trithiocyanates*, $\text{KHg}(\text{SCN})_3$, $\text{NH}_4\text{Hg}(\text{SCN})_3$, and $\text{Ba}[\text{Hg}(\text{SCN})_3]_2 \cdot 2\text{H}_2\text{O}$, are well crystallised salts, insoluble in cold water, but easily soluble in hot water whereby they are decomposed into mercury thiocyanate and the tetrathiocyanate.

Mercury tetrathiocyanates.—The *potassium* salt, $\text{K}_2\text{Hg}(\text{SCN})_4$, obtained by crystallising a mixture of the constituent salts, crystallises in white needles and is easily soluble in water and alcohol. The *sodium* and *barium* salts are similar. The *copper* salt, $\text{CuHg}(\text{SCN})_4$, obtained by treating a solution of the alkali salt with copper chloride or nitrate, crystallises from boiling water in intensely green, microscopic

tablets and is insoluble in cold water or alcohol. The electrical conductivity of both the trithiocyanates and the tetrathiocyanates shows that they are salts of a complex acid, as also does their behaviour in Nernst's apparatus for demonstrating the movement of the ions.

Cobalt thiocyanate, $\text{Co(SCN)}_2 \cdot 3\text{H}_2\text{O}$, obtained by dissolving cobalt carbonate in thiocyanic acid, crystallises in violet, rhombic tablets [$a:b:c = 1.2302:1.05824$], and gives a blue solution in water and alcohol which turns pink on dilution. The *double salts*, $\text{K}_2\text{Co(SCN)}_4 \cdot 4\text{H}_2\text{O}$; $\text{Na}_2\text{Co(SCN)}_4 \cdot 8\text{H}_2\text{O}$ ($\text{NH}_4)_2\text{Co(SCN)}_4 \cdot 4\text{H}_2\text{O}$, and $\text{BaCo(SCN)}_4 \cdot 8\text{H}_2\text{O}$, are obtained by adding the corresponding thiocyanate to a solution of the cobalt salt. They crystallise in beautiful, dark blue needles, can be recrystallised from water or alcohol, are soluble in methyl, ethyl, or amyl alcohol, acetone or wet ether, and give deep blue solutions which on dilution turn bright rose colour. The *silver salt*, $\text{Ag}_2\text{Co(SCN)}_4$, is obtained by titrating a concentrated alcoholic solution of the potassium salt with freshly precipitated silver thiocyanate.

Nickel thiocyanate, $\text{Ni(SCN)}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, is a yellowish-brown, crystalline powder and gives a green solution in water. The *potassium*, *sodium*, and *ammonium* double salts are crystalline, hygroscopic salts easily soluble in water or hot alcohol with a green colour, and by solution in water are decomposed into their components. *Barium* and *silver* salts cannot be obtained. They are insoluble in most organic solvents and do not behave like salts of a complex acid. This difference in the behaviour of the cobalt and nickel salts explains Vogel's qualitative test for cobalt in the presence of nickel.

Potassium chromium thiocyanate, $\text{K}_2\text{Cr(SCN)}_6 \cdot 4\text{H}_2\text{O}$, and the sodium salt, with $12\text{H}_2\text{O}$, obtained according to Roesler's method (*Annalen*, 1867, 141, 185), have an electrical conductivity which points to their being salts of the complex group Cr(SCN)_6 .

An examination of the iron double thiocyanates shows that two series of salts are formed, namely, ferrihexathiocyanates and ferrohexathiocyanates, which correspond respectively with the ferri- and ferro-cyanides.

Sodium ferrithiocyanate, $\text{Na}_3\text{Fe(SCN)}_6 \cdot 12\text{H}_2\text{O}$, obtained by allowing a solution of the constituent thiocyanates to crystallise over sulphuric acid, forms dark green, hexagonal or rhombic crystals, is decomposed by alkali hydroxides with the formation of ferric hydroxide, dissolves in absolute alcohol to a violet solution resembling permanganate, from which it separates without decomposition; with water, it yields the well known deep red solution, and is partially decomposed, and with ether is decomposed into its constituents, whereby the ferric thiocyanate is dissolved. The *potassium* and *ammonium* salts crystallise with $4\text{H}_2\text{O}$.

Sodium ferrothiocyanate, $\text{Na}_4\text{Fe(SCN)}_6 \cdot 12\text{H}_2\text{O}$, obtained by dissolving ferrous carbonate in thiocyanic acid and adding to the solution sodium thiocyanate, crystallises in colourless tablets, dissolves in water and alcohol with a bright rose coloration, and is oxidised by exposure to the air. The *potassium* and *ammonium* salts are bright red, micro-crystalline salts and are extremely hygroscopic.

An examination of the ferrihexathiocyanates in Nernst's apparatus shows that the violet absolute alcoholic solution contains the complex

$\text{Fe}(\text{SCN})_3$, whilst the blood red solutions do not contain a complex anion. These results show that the red coloration obtained on adding a ferric salt to a thiocyanate is due to the presence of ferric thiocyanate, and not to the formation of a complex double salt.

Potassium aluminium thiocyanate, $\text{K}_3\text{Al}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$, obtained in a similar manner to the iron salt, crystallises in colourless crusts, is very hygroscopic, and easily soluble in water or alcohol. E. C. R.

Methylenemalonamide and Methylenebiuret. By HUGO SCHIFF (*Annalen*, 1901, 316, 242—249).—*Methylenemalonamide*, $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_4$, obtained by the action of formaldehyde on malonamide, has one or other of the following formulæ, $\text{CH}_2:\text{C}(\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH})_2$ or $\text{CH}_2<\text{O}\cdot\text{CH}_2>\text{C}(\text{CO}\cdot\text{NH}_2)_2$, the second being more in accordance with the behaviour of the compound. The substance slowly evolves ammonia when treated with cold potassium hydroxide, it gives the biuret reaction, and when treated with mercuric nitrate and potassium hydroxide, yields three *mercurides*, having the following composition, $\text{Hg}(\text{C}_6\text{H}_9\text{O}_4\text{N}_2)_2$, $\text{Hg}(\text{C}_6\text{H}_8\text{O}_4\text{N}_2)$ and $\text{Hg}_2(\text{C}_6\text{H}_7\text{O}_4\text{N}_2)_3$.

Methylenebiuret, $\text{CH}_2[\text{O}\cdot\text{CH}_2\cdot\text{N}(\text{CO}\cdot\text{NH}_2)_2]_2$, prepared by gradually adding formaldehyde to a saturated alcoholic solution of biuret heated at 50° is obtained as an amorphous, colourless, pasty mass; it gives the biuret reaction and unstable *mercurides* varying in composition from $\text{Hg}_3(\text{C}_7\text{H}_{11}\text{O}_6\text{N}_6)_2$ to $\text{Hg}_2(\text{C}_7\text{H}_{10}\text{O}_6\text{N}_6)$. The paper includes a description of a method for estimating mercury in organic compounds. G. T. M.

Methyl Cyanide as a Catalytic Reagent; and a Criticism of J. U. Nef's views on the Frankland, Wurtz, and Conrad Reactions. By ARTHUR MICHAEL (*Amer. Chem. J.*, 1901, 25, 419—430).—If, in the preparation of hydrocarbons by the action of sodium on alkyl haloids, a few drops of acetonitrile are added, the necessity for heating in a sealed tube is avoided, and the yield of the product is increased. On addition of acetonitrile to a well-cooled mixture of methyl iodide and sodium, an energetic reaction occurs; when ethyl or propyl iodide is treated at the ordinary temperature with sodium in presence of the nitrile, a good yield of butane or *n*-hexane is obtained. Allyl iodide, *isopropyl* iodide, trimethylene bromide and benzyl chloride behave in a similar manner. The acetonitrile may be replaced by propionitrile or butyronitrile, which, however, exert a less marked influence; benzonitrile and phenylacetonitrile cause no acceleration of the reaction.

When ethylene bromide is boiled with zinc-sodium, no action takes place; in presence of ethyl oxalate, however, at a temperature of 40° , gas is rapidly evolved and ethyl bromide produced.

If zinc ethyl iodide, prepared by heating a mixture of zinc, ethyl iodide, and ether on the water-bath, is treated with an ethereal solution of benzoyl chloride, phenyl ethyl ketone is formed, together with a product boiling at 193 — 196° under 9 mm. pressure, and a small quantity of a white, crystalline substance. The author has also studied the action of zinc ethyl iodide on ethyl malonate, and obtained ethyl ethylmalonate and a little ethyl diethylmalonate; the last-

mentioned substance forms an additive compound with zinc ethyl iodide.

The paper concludes with a criticism of Nef's views on the Frankland, Wurtz, and Conrad reactions. E. G.

Constitution of the Compounds of Ethylene and Allyl Alcohol with Mercuric Salts. By JULIUS SAND (*Ber.*, 1901, 34, 1385—1394. Compare *Abstr.*, 1900, i, 384, 386, 618).—Ethanolmercuric iodide, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgI}$, was obtained in the same manner as the corresponding chloride and bromide. When it is boiled with iodine, either in aqueous potassium iodide or in alcoholic solution, mercuric iodide and glycol iodohydrin (Henry, *Bull. Acad. roy. Belg.*, 1889, [iii], 18, 182) are formed. The latter boils at 78° under 16 mm. pressure; when heated with quinoline at 100° , it forms a yellow *quinolinium iodide*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_9\text{H}_7\text{NI}$, which melts at 157° , and can be converted into the corresponding *chloride*, a colourless, deliquescent substance melting at 122° . Ethanolmercuric iodide forms a *benzoyl* derivative melting at 118° ; this, unlike the parent substance, is not decomposed readily by hydrochloric acid with evolution of ethylene. Acetic anhydride does not convert ethanolmercuric bromide into a corresponding acetyl derivative; monobromomercuriacetic acid, melting at 117 — 118° , is obtained instead.

Ethyl ether mercuric iodide, $\text{O}(\text{CH}_2\cdot\text{CH}_2\cdot\text{HgI})_2$, was obtained by passing ethylene into aqueous mercuric sulphate, dissolving the precipitate in aqueous potassium hydroxide, and precipitating with potassium iodide. It is an oil which decomposes when distilled even under diminished pressure. With quinoline, it forms a reddish-yellow *monoquinolinium* and a red *diquinolinium* salt, $\text{I}\cdot\text{C}_9\text{H}_7\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$ and $\text{O}(\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_9\text{H}_7\text{NI})_2$, melting at 176° and 254° , in the latter case with decomposition, and respectively more and less soluble in alcohol.

Propylene glycol mercuric iodide, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{HgI}$, does not crystallise readily; iodine converts it even at 40° into a liquid iodohydrin, and it forms a *dibenzoyl* derivative which melts at 100° and is stable to hydrochloric acid, although acetic acid decomposes the parent substance into allyl alcohol and mercuric salt.

The substance described as propenolmercuric iodide, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{HgI}$, is obtained by treating aqueous mercuric nitrate solution alternately with potassium hydroxide and allyl alcohol, precipitating with potassium iodide, and recrystallising from 20 per cent. aqueous potassium hydroxide. When heated with iodine and benzene at 140° , it yields mercuric iodide and di-epiiodohydrin (Stoehr, *Abstr.*, 1897, i, 262). As this has the constitution

$\text{CH}_2\text{I}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{O}\\\text{O}\cdot\text{CH}_2\end{smallmatrix}\right\rangle\text{CH}\cdot\text{CH}_2\text{I}$, the original iodide must have been di-

propylene oxide mercuric iodide, $\text{HgI}\cdot\text{CH}_2\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{O}\\\text{O}\cdot\text{CH}_2\end{smallmatrix}\right\rangle\text{CH}\cdot\text{CH}_2\cdot\text{HgI}$.

When an alkaline solution of ethanolmercuric bromide is treated with alkaline stannous chloride solution, a volatile, poisonous mercury compound is formed, probably *mercury dihydroxydiethyl*, $\text{Hg}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$. C. F. B.

Hydrogenation of Aromatic Hydrocarbons. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1901, 132, 1254—1257).—The action of reduced nickel below 250° on mixtures of aromatic hydrocarbons and hydrogen (this vol., i, 195 and 263) is simple in the case of benzene and its methyl derivatives, and the sole product is the corresponding *cyclohexane*, but if ethyl, propyl, *isopropyl*, and other longer chains have been inserted in the benzene molecule the reaction is more complicated, and small quantities of lower homologues are formed with the principal product. *cycloHexane* itself has an odour recalling those of chloroform and oil of roses; it melts at 6.5° , boils at 81° under 755 mm. pressure, and has a sp. gr. 0.7808 at 18.7° . The other *cyclohexanes* prepared were as follows:

| | B. p. corr. | Sp. gr. at $0^{\circ}/4^{\circ}$. |
|---|-----------------|------------------------------------|
| Methyl <i>cyclohexane</i> | 100.1° | 0.7859 |
| 1:2-Dimethyl <i>cyclohexane</i> | 126 | 0.8008 |
| 1:3-Dimethyl <i>cyclohexane</i> .. | 121 | 0.7874 |
| 1:4-Dimethyl <i>cyclohexane</i> | 120 | 0.7866 |
| Ethyl <i>cyclohexane</i> | 130 | 0.8025 |
| 1:3:5-Trimethyl <i>cyclohexane</i> | 137—139 | 0.7884 |
| 1:3:4-Trimethyl <i>cyclohexane</i> | 143—144 | 0.8052 |
| 1-Methyl-4-ethyl <i>cyclohexane</i> | 150 | 0.8041 |
| Propyl <i>cyclohexane</i> | 153—154 | 0.8091 |
| 1-Methyl-4- <i>isopropylcyclohexane</i> ... | 169—170 | 0.8132 |

The sp. gr. is less than that of the corresponding benzene hydrocarbon, but the difference is lower the more complex the molecule.

Styrene in presence of nickel is completely converted into ethyl*cyclohexane*. Further, reduced copper at 180° in presence of hydrogen converts it into ethylbenzene (compare Abstr., 1900, i, 469), whilst with reduced cobalt, intermediate in energy between copper and nickel, the product is a mixture of ethylbenzene and ethyl*cyclohexane*.

Under the same conditions, the quadrivalent terpenes, such as limonene, sylvestrene, and terpinene, yield 1-methyl-4-*isopropylcyclohexane*, as also does menthene. Terebenthene and *l*-camphene, on the other hand, yield two isomeric hydrocarbons of the composition $C_{10}H_{18}$. The product from the first boils at 166° (corr.), and has a sp. gr. 0.862 at $0^{\circ}/4^{\circ}$, and that from the second boils at 164 — 165° (corr.), and has a sp. gr. 0.849 at $0^{\circ}/4^{\circ}$.

Naphthalene at 200° yields solely the tetrahydride, $C_{10}H_{12}$, boiling at 205° (corr.), and having a sp. gr. 0.9825 at $0^{\circ}/4^{\circ}$. Acenaphthene behaves similarly, but the product boils at 254° (corr.), and is identical with the reduction product obtained by Bamberger and Lodter by the action of hydrogen iodide.

C. H. B.

Electrochemical reduction of Aromatic Mononitro-compounds to Amines. By KARL ELBS and F. SILBERMANN (*Zeit. Elektrochem.*, 1901, 7, 589—591).—At a zinc cathode or in presence of a zinc salt, nitrobenzene and its homologues are reduced mainly to the corresponding amines. Similar results are obtained with a lead cathode, the yields being rather better (80 to 90 per cent.). T. E.

Aromatic Nitro-compounds. XIV. Action of Potassium Cyanide on 1-Chloro-2:4-dinitrobenzene in Alcoholic Solution. By W. J. VAN HETEREN (*Rec. Trav. Chim.*, 1901, 20, 107—110. Compare Lobry de Bruyn, *Abstr.*, 1885, 656, 657; 1895, i, 654).—When 1-chloro-2:4-dinitrobenzene is heated with aqueous potassium cyanide in ethyl alcoholic solution at 40°, the temperature rises to 60°, and a dark-brown, amorphous precipitate is formed, from which a small quantity (5 per cent.) of a *chloronitrocycanoethoxybenzene* (probably $\text{OEt}:\text{CN}:\text{NO}_2:\text{Cl}=1:2:3:4$ or $1:2:3:6$, compare *loc. cit.*) can be isolated; it separates from alcohol in nearly colourless crystals and melts at 112°. Using methyl alcohol, the analogous *chloronitrocyanomethoxybenzene* is obtained in similar yield; it crystallises from alcohol in nearly colourless leaflets and melts at 163°. W. A. D.

Aromatic Nitro-compounds. XV. Replacement of the Nitro-group by Methoxyl in 1-Chloro-3:5-dinitrobenzene. By A. C. DE KOCK (*Rec. Trav. Chim.*, 1901, 20, 111—114).—Details are given for preparing 3:5-dinitroaniline from trinitrobenzene by reduction with ammonium sulphide; 1-chloro-3:5-dinitrobenzene, obtained from it by Sandmeyer's reaction, when boiled with sodium methoxide in methyl alcoholic solution for an hour, yields about 10 per cent. of its weight of 3-chloro-5-nitro-1-methoxybenzene, which separates from dilute alcohol in small, white crystals and melts at 91°. No well-defined product could be obtained by using sodium ethoxide in ethyl alcoholic solution instead of the methoxide in this interaction. W. A. D.

Aromatic Nitro-compounds. XVI. Comparative Study of the three Dinitrobenzenes. III. Action of Sodium Monosulphide. By CORNELIS A. LOBRY DE BRUYN and J. J. BLANKSMA (*Rec. Trav. Chim.*, 1901, 20, 115—120. Compare *Abstr.*, 1900, i, 226).—When *o*-dinitrobenzene is boiled with an alcoholic solution of sodium monosulphide (1 mol.), *o*-nitrothiophenol seems to be formed, but cannot be isolated; using 2 mols. of the monosulphide, 1:1'-dinitrodiphenylsulphide is formed, which is oxidised at the ordinary temperature by nitric acid of sp. gr. 1.5 to the *sulphoxide*, $(\text{NO}_2\cdot\text{C}_6\text{H}_4)_2\text{SO}$. This separates from alcohol in yellow crystals, melts at 184°, and is further oxidised by boiling nitric acid to 1:1'-dinitrodiphenylsulphone (Gericke, *Annalen*, 1856, 100, 211; Colby and McLoughlin, *Abstr.*, 1887, 371).

In alcoholic solution, sodium monosulphide principally reduces *m*-dinitrobenzene to *m*-nitroaniline, but di-*m*-nitroazoxybenzene is also formed along with sodium thiosulphate and amorphous products (compare this vol., i, 461); from *p*-dinitrobenzene, di-*p*-nitroazobenzene is formed along with an amorphous powder insoluble in glacial acetic acid. W. A. D.

Substitutions and Transformations effected by Sodium Disulphide. By J. J. BLANKSMA (*Rec. Trav. Chim.*, 1901, 20, 121—140).—A full account of work formerly dealt with in brief (*Abstr.*, 1900, i, 226 and 442); in all the following cases, the substance taken was boiled with

alcoholic sodium disulphide for periods varying from a few minutes to one or two hours. *p*-Chloronitrobenzene and *p*-iodonitrobenzene both yield di-*p*-nitrophenyl disulphide which melts at 170°, the melting point not being raised by several crystallisations, although when prepared from *p*-nitrothiophenol it melts, as stated by Willgerodt (Abstr., 1885, 519), Bamberger and Kraus (Abstr., 1896, i, 218), and Kehrmann and Bauer (Abstr., 1897, i, 27), at 181°; it is remarkable for exploding to a fine powder at 134°, this temperature being evidently a point of transition of crystalline form. On oxidation with nitric acid of sp. gr. 1.5, it yields *p*-nitrobenzenesulphonic acid, which forms long hygroscopic crystals, melts at 95°, and yields a *sulphochloride* crystallising from ether and melting at 76°, and a *sulphonamide* crystallising from water and melting at 178°; Limpricht (this Journal, 1875, 1027) describes the sulphochloride as a red oil and the sulphonamide as melting at 131°.

1:4-Dichloro-2-nitrobenzene yields 4:4'-dichloro-2:2'-dinitrodiphenyl disulphide which melts at 212°, and was formerly described by Beilstein and Kurbatow (Abstr., 1878, 139) as chloronitrophenylmercaptan; on oxidation with nitric acid, it yields 4-chloro-2-nitrobenzenesulphonic acid, the *sulphochloride* of which forms white crystals and melts at 78—79°. 4:4'-Dibromo-2:2'-dinitrodiphenyl disulphide, obtained from 1:4-dibromo-2-nitrobenzene, forms yellow crystals, melts at 174°, and yields on oxidation a hygroscopic 4-bromo-2-nitrobenzenesulphonic acid melting at 126°; the *sulphochloride* is white and melts at 100°. 2:2'-Dinitro-5:5'-dichlorodiphenyldisulphide, obtained from 1-chloro-3:4-dinitrobenzene as principal product, forms yellow crystals and melts at 171°; a small quantity of a *substance* melting at 151° is also formed.

Allyl disulphide is a yellow oil which boils at 100° under 80 mm., and at 174° with decomposition under the ordinary pressure; it has a sp. gr. 1.010 at 15°, and combines additively with 2 mols. of bromine to form a thick oil which is decomposed by atmospheric moisture.

Ethylene bromide yields a white, amorphous compound, $(C_2H_4S_2)_n$, which melts at 113°, and is not identical with Fasbender's diethylene tetrasulphide (Abstr., 1888, 805), although, like the latter, it yields ethylenedisulphonic acid on oxidation with nitric acid.

Fluorescein chloride yields a *disulphide*, $C_{20}H_{10}O_3S_2$, as a greyish powder which does not melt at 300°. W. A. D.

Reducing Action of Sodium Disulphide. Preparation of Di-*m*-nitroazoxybenzene and of Di-*p*-nitroazobenzene. By J. J. BLANKSMA (*Rec. Trav. Chim.*, 1901, 20, 141—143).—On boiling *m*-dinitrobenzene (2 mols.) with sodium disulphide in alcoholic solution, sodium thiosulphate and a nearly theoretical yield of di-*m*-nitroazoxybenzene are obtained; the abnormal action of sodium monosulphide on *m*-dinitrobenzene (de Bruyn and Blanksma, this vol., i, 460) is probably due to the monosulphide used being in this case initially transformed into sodium disulphide and hydroxide, the latter being responsible for the amorphous substance formed. In the case of *p*-dinitrobenzene, di-*p*-nitroazobenzene is the principal product along with sodium thiosulphate. W. A. D.

Formation of Organic Tri- and Tetra-sulphides. By J. J. BLANKSMA (*Rec. Trav. Chim.*, 1901, 20, 144—145. Compare this vol., i, 264).—2:2'-Dinitrodiphenyl trisulphide, obtained by boiling *o*-dinitrobenzene (2 mols.) with alcoholic sodium trisulphide, made by dissolving sodium disulphide (1 mol.) and sulphur (1 atom) in alcohol, crystallises from alcohol in yellow, silky needles and melts at 185°. Using sodium tetrasulphide (sodium disulphide + 2 atoms of sulphur), *di-o-nitrophenyl tetrasulphide* is obtained in yellow needles, which crystallise from alcohol and melt at 160°; the same tetrasulphide is formed by the action of iodine on *sodium nitrodithiophenoxide*, which is present in a cold alcoholic solution of *o*-dinitrobenzene and sodium disulphide. W. A. D.

Aromatic Dicarbylamines. By FELIX KAUFLEDER (*Ber.*, 1901, 34, 1577—1579. Compare Grassi-Cristaldi and Lambardi, *Abstr.*, 1895, i, 568).—Aromatic dicarbylamines may be readily obtained by treating aromatic diamines with concentrated aqueous potassium hydroxide and excess of chloroform. By this means the carbylamine dissolves in the excess of chloroform and is protected from the decomposing action of the alkali.

p-Phenylenedicarbylamine, $C_6H_4(NC)_2$, crystallises in colourless needles, has an obnoxious odour, turns black at 130—140° and is partly transformed into the nitrile, a conversion which takes place readily at 230—260°. The *tetrabromide* melts at 137—138°. *m*-Phenylenedicarbylamine crystallises in colourless needles, turns to a brownish-black amorphous mass on exposure to the air, blackens at 75°, and gives off a gas at 90—95°. J. J. S.

Constitution of Acylhalogenalkylamides. By JULIUS STIEGLITZ and E. E. SLOSSON (*Ber.*, 1901, 34, 1613—1616. Compare Norton and Tcherniac, *Abstr.*, 1878, 971; Armstrong, *Trans.*, 1900, 77, 1047; Chattaway, *ibid.*, 1899, 75, 1046; Comstock, *Abstr.*, 1890, 1414).—Acetylchloroaniline is reduced by the action of potassium cyanide to acetanilide and thus does not react similarly to dialkylchloroamines, R_2NCl , or chloropiperidine, in which the halogen becomes replaced by cyanogen. Zinc alkyl compounds also reduce the *N*-chloroanilides and do not alkylate them as in the case of dichloroethylamine (Tcherniac, *this Journ.*, 1876, i, 903).

Benzoylchloroamide and diazomethane yield the *O*-ether, methyl chloroiminobenzoate (*Abstr.*, 1897, i, 43).

Acetylchloroamylamine, which is formed when acetylamine is treated with hypochlorous acid, may also be obtained by the acetylation of chloroamylamine, and must therefore have the constitution $C_5H_{11} \cdot NClAc$. Comstock's formulæ must be rejected. J. J. S.

Oxidation of Nitrous Acid and Nitrosoamines. By DANIEL VORLÄNDER (and, in part, RUDOLF VON SCHILLING and M. SCHRÖDTER) (*Ber.*, 1901, 34, 1642—1646. Compare this vol., i, 444).—Nitrites differ from nitrous acid in their stability towards potassium permanganate. There is no such difference between sulphurous acid and normal sulphites. The latter are partly hydrolysed in solution and contain acid sulphite. In nitrous and sulphurous acids and the acid sulphites, there

is a hydrogen atom in position 3 relatively to the unsaturated linking, for example, $\text{H}\cdot\text{O}\cdot\ddot{\text{N}}\cdot\text{O}$, and $\text{HO}\cdot\ddot{\text{S}}\cdot\text{O}\cdot\text{ONa}$ (compare *loc. cit.*). For the same reason, the nitroso-derivatives of secondary aromatic amines are not oxidised to nitroamines by alkaline potassium permanganate, but to nitrosoalkylaminobenzoic acids. Thus, nitrosomethyl-*o*-toluidine can be oxidised to nitrosomethylanthranilic acid; and nitrosoethyl-*o*-toluidine and nitrosoethyl-*m*-toluidine can be oxidised respectively to nitrosoethylanthranilic and nitrosoethyl-*m*-aminobenzoic acids (m. p. 133—135°).

Ethyl o-methylaminobenzoate melts at 39°, and boils at 172—175° under 45 mm. pressure. *Methyl o-ethylaminobenzoate* is a pleasant smelling oil boiling at 148—150° under 45 mm. pressure. *Nitroso-o-tolylglycine*, prepared from *o*-tolylglycine, melts at 44—45°, and is oxidised to *nitrosophenylglycine-o-carboxylic acid*, which forms a colourless, crystalline precipitate melting and decomposing at 120°.

K. J. P. O.

Oxidation of Arylaminodiacetic Acids. By DANIEL VORLÄNDER and ERICH MUMME (*Ber.*, 1901, **34**, 1647—1649).—Anilino- and *o*-toluidino-diacetic acids can both be easily titrated as dibasic acids, and give colour reactions with ferric chloride and thus contrast with anildiacetic-*o*-carboxylic acid (this vol., i, 83). The *hydrochloride* of anilindiacetic acid, prepared by the action of hydrogen chloride on a solution of the acid in acetone, is decomposed by water. As was to be expected (compare preceding abstract and this vol., i, 454), oxidation with alkaline potassium permanganate at the ordinary temperature converts these acids very readily into oxalic acid and formylphenylglycine and *formyl-o-tolylglycine* respectively; the latter crystallises in prisms from water, and melts at 113—114°.

K. J. P. O.

Action of Nitrous Acid on *o*-Toluidinodiacetic Acid. By DANIEL VORLÄNDER and RUDOLF VON SCHILLING (*Ber.*, 1901, **34**, 1649—1651).—*o*-Toluidinodiacetic acid is converted by nitrous acid into nitroso-*o*-tolylglycine, formaldehyde, and carbon dioxide. Glyoxylic acid is not an intermediate product in the formation of formaldehyde by the oxidation, as nitrous acid does not convert glyoxylic acid into the aldehyde.

The glyoxylic acid compound, with dimethylhydroresorcinol, $\text{C}_{18}\text{H}_{24}\text{O}_6$, forms needles melting at 210—212°, which contain water; the anhydrous compound melts at 230°.

K. J. P. O.

Action of Hydrogen Chloride on Nitroso-*o*-tolylglycine. By DANIEL VORLÄNDER and M. SCHRÖDTER (*Ber.*, 1901, **34**, 1651—1653).—By the action of dry hydrogen chloride on alcoholic, ethereal, or acetic acid solutions of nitroso-*o*-tolylglycine, the *hydrochloride* of a chlorotolylene-*p*-diamine, $\text{C}_7\text{H}_9\text{N}_2\text{Cl}\cdot 2\text{HCl}$, is obtained as colourless crystals. The *sulphate*, $\text{C}_7\text{H}_9\text{N}_2\text{Cl}\cdot \text{H}_2\text{SO}_4$, forms white, insoluble crystals; the *base*, $\text{C}_6\text{H}_2\text{MeCl}(\text{NH}_2)_2$, crystallises in white scales melting at 146°; the *diacetyl* derivative in white needles melting above 300°. The base is very readily oxidised to a chlorotoluquinone melting at 102° (compare Schniter, *Abstr.*, 1887, 1036), which yields a quinol melting at 175°.

K. J. P. O.

9-Aminophenanthrene. By JULIUS SCHMIDT and MAX STROBEL (*Ber.*, 1901, **34**, 1461—1467. Compare this vol., i, 76).—9-Aminophenanthrene, $C_{14}H_{11}N$, prepared by reducing 9-nitrophenanthrene (*loc. cit.*) with tin and hydrochloric acid, melts at $135\text{--}136^\circ$ [Japp and Findlay give 139°], and sublimes without decomposition; it is identical with an aminophenanthrene which Pschorr (unpublished results) has prepared from 9-phenanthrenecarboxylic acid, but differs from J. A. Schmidt's liquid product (*Abstr.*, 1879, 941). The hydrochloride forms silvery white prisms, is only very slightly soluble in water, from which it separates in needles and melts at 275° , with liberation of gas. The *picrate* separates slowly from an alcoholic solution in the form of green needles, becomes yellow at about 125° , darkens at about 180° , and melts, with liberation of gas, at 190° ; from hot alcoholic or aqueous solution, it separates in yellow needles. The *acetyl* derivative crystallises from alcohol in small, white needles, sinters at 205° , and melts at $207\text{--}208^\circ$ to a brown liquid. The *benzoyl* derivative crystallises from alcohol in white, silky needles, melts sharply at 199° to a clear liquid, and is the most suitable derivative for identifying the base. 9-Phenanthrylurethane, $C_{14}H_9 \cdot NH \cdot CO_2Et$, crystallises from alcohol in glistening, white needles and melts at $156\text{--}158^\circ$. Benzylideneaminophenanthrene, $C_{14}H_9 \cdot N : CHPh$, crystallises from alcohol in yellow prisms and melts at $108\text{--}109^\circ$ to a yellow liquid. *s*-Phenanthrylphenylcarbamide, $C_{14}H_9 \cdot NH \cdot CO \cdot NHPh$, is insoluble in most solvents, but can be purified by boiling with alcohol, sinters at 260° , and melts, with liberation of gas, at 290° . *s*-Phenanthrylphenylthiocarbamide, $C_{14}H_9 \cdot NH \cdot CS \cdot NHPh$, separates from benzene in small, white crystals, is very slightly soluble in most solvents, and melts at $194\text{--}195^\circ$ to a pale yellow liquid. T. M. L.

NOTE.—No reference is made to the earlier preparation of 9-aminophenanthrene (β -phenanthrylamine) by Japp and Findlay (*Trans.*, 1897, **71**, 1123) by the action of ammonia on phenanthrene. EDITORS.

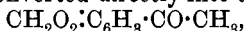
Constitution of Mononitrosoorcinol. By FERDINAND HENRICH (*Monatsh.*, 1901, **22**, 232—252. Compare *Abstr.*, 1897, i, 446, and 1900, i, 163).—On treating orcinol with methyl iodide and sodium ethoxide in alcoholic solution, a mixture of methyl derivatives is formed, from which the monomethyl ether can be isolated by fractional distillation. A fraction of higher boiling point contains a substance which with nitrous acid yields a nitroso-derivative insoluble in benzene, and forming yellow needles melting at $160\text{--}165^\circ$. The aminophenol obtained by reducing the monomethyl ether of nitrosoorcinol yields a *benzoyl* derivative, $NHBz \cdot C_6H_2Me(OMe) \cdot OH$, which crystallises in long needles melting at $216\text{--}218^\circ$. On heating the latter at 230° for many hours, *methoxy-1-phenylmethylbenzoxazole*, $OMe \cdot C_6H_2Me < \begin{smallmatrix} N \\ \diagup \diagdown \\ O \end{smallmatrix} > CPh$, is obtained with elimination of H_2O . It crystallises in prisms from alcohol and melts at $96\text{--}97.5^\circ$. The substance was synthesised from hydroxy-1-phenylmethylbenzoxazole.

Nitroso-orcinol ethyl ether, $OEt \cdot C_6H_2MeO \cdot NOH$, prepared from nitroso-orcinol by the action of alcoholic hydrogen chloride, crystallises in dark red prisms from alcohol and melts at $113\text{--}114^\circ$. This sub-

stance was also prepared by the action of nitrous acid on orcinol ethyl ether.
K. J. P. O.

Synthetical application of Mercury Fulminate. **Synthesis of Phenol Aldoximes.** By ROLAND SCHOLL and ERNST BERTSCH (*Ber.*, 1901, 34, 1441—1446).—The following method for preparing the aldoximes of polyhydric phenols is applicable in all cases in which there are two hydroxyl groups in the meta-position to one another and a free para-position. Mercury fulminate is suspended in an ethereal solution of the phenol and hydrogen chloride passed into the liquid, which must be kept cool. The method has been applied to the preparation of β -resorcylic, orcylic, phloroglucylic and pyrogallol-aldoximes. The last-named compound melts at 161—162°, whilst Gattermann (*Abstr.*, 1898, i, 581) gave 157—158° for the compound $C_6H_2(OH)_3 \cdot CHO$ [OH : OH : OH : CHO = 1 : 2 : 3 : 4]. T. H. P.

Synthesis of Acetylpiperone. By W. FEUERSTEIN and M. HEIMANN (*Ber.*, 1901, 34, 1468—1472).—*Methyl piperonylacrylate*, $CH_2 \begin{smallmatrix} \diagup O \diagdown \end{smallmatrix} C_6H_3 \cdot CH : CH \cdot CO_2Me$ [CH : O₂ = 1 : 3 : 4], crystallises from dilute methyl alcohol in large tablets and melts at 68—69°. The *ethyl* ester forms long needles and melts at 67—68°. The *dibromide* of piperonylacrylic acid, $CH_2O_2 \cdot C_6H_3 \cdot CHBr \cdot CHBr \cdot CO_2H$, crystallises from chloroform and melts at 143—144° with liberation of gas. *Methylenedioxybromostyrene*, $CH_2O_2 \cdot C_6H_3 \cdot CH : CHBr$, prepared from the preceding compound, crystallises from dilute methyl alcohol in white needles and melts at 59°. *Piperonylacetylene*, $CH_2O_2 \cdot C_6H_3 \cdot C \equiv CH$, prepared by heating the preceding compound with potassium hydroxide, was not isolated but was converted directly into the yellow *silver* derivative; the latter was heated with alcohol and hydrochloric acid and converted directly into acetylpiperone,



which was found to be identical with Jobst and Hesse's '*p*-coumarhydrin' (*Abstr.*, 1880, 325), thus confirming the conclusions of Ciamician and Silber (*Abstr.*, 1892, 873) as to the nature of the latter substance. *o*-Hydroxybenzylideneacetylpiperone, $CH_2O_2 \cdot C_6H_3 \cdot CO \cdot CH : CH \cdot C_6H_4 \cdot OH$, prepared by the action of sodium hydroxide on an alcoholic solution of acetylpiperone and salicylaldehyde, crystallises from alcohol in yellow needles and melts at 162—163°. T. M. L.

The Fluorescent Substance derived from Ethyl 2-Bromo-*a*-naphthaquinone-3-acetoacetate. By CARL T. LIEBERMANN and THEODOR LANSER (*Ber.*, 1901, 34, 1543—1553).—The fluorescent substance formed by the action of alcoholic potash on ethyl bromonaphthaquinoneacetoacetate (*Abstr.*, 1900, i, 311), has apparently the constitu-

tion $CO \begin{smallmatrix} \diagup C_6H_4 \cdot C(OH) \cdot CH \\ \diagdown CBr = C \cdot CH_2 \cdot C \cdot OH \end{smallmatrix}$ (I), but its properties are also in accord

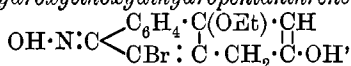
with the isodynamic formulæ, $OH \cdot C \begin{smallmatrix} \diagup C_6H_4 \cdot C(OH) \cdot CH \\ \diagdown CBr = C \cdot CH = C \cdot OH \end{smallmatrix}$ (II) and

$CO \begin{smallmatrix} \diagup C_6H_4 \cdot C(OH) \cdot CH_2 \\ \diagdown CBr = C \cdot CH_2 \cdot CO \end{smallmatrix}$ (III). To the parent hydrocarbon nucleus

$C_{13}H_{10}$, $CH \leq \begin{matrix} C_6H_4 \cdot CH - CH \\ CH - C : CH \cdot CH \end{matrix}$, the name *pentanthrene* is given. The fluorescence is attributed to the hydroxyl group attached to the tertiary carbon atom present, owing to the fact that when this radicle is etherified (*loc. cit.*) or replaced by halogens (*infra*), derivatives are obtained which are not fluorescent.

Bromodiaceoxymethoxypentanthrene, $OAc \cdot C \leq \begin{matrix} C_6H_4 \cdot C(OMe) \cdot CH \\ CBr - C : CH - C \cdot OAc \end{matrix}$, obtained by acetylating the methyl ether of the fluorescent substance, crystallises from benzene in colourless leaflets and melts at $189-191^\circ$. The fluorescent substance itself yields with acetic anhydride at $55-60^\circ$ the compound, $C_{26}H_{19}O_7Br$, formed by the acetylation of 1 mol. of the form III and elimination of hydrogen bromide (1 mol.) between the bromine atom of the product and the hydroxyl group of the same form.

Bromoketoximohydroxyethoxydihydropentanthrene,



is obtained by the action of hydroxylamine hydrochloride on either the ethyl ether of the fluorescent substance, or the latter itself dissolved in alcohol, when etherification spontaneously occurs; it crystallises from alcohol in yellow needles and is soluble in cold alkalis.

Dibromodihydroxypentanthrene, $OH \cdot C \leq \begin{matrix} C_6H_4 \cdot CBr \cdot CH \\ CBr - C = CH \end{matrix} > C \cdot OH$,

formed at the ordinary temperature on adding hydrobromic acid of sp. gr. 1.49 to a solution of the fluorescent substance in glacial acetic acid, crystallises from dilute alcohol in colourless leaflets and melts and decomposes at 174° .

Chlorobromodihydroxypentanthrene, $OH \cdot C \leq \begin{matrix} C_6H_4 \cdot CCl \cdot CH \\ CBr - C = CH \end{matrix} > C \cdot OH$,

obtained similarly, using hydrochloric acid, melts and decomposes at $173-174^\circ$, and when mixed with aqueous potassium iodide in alcoholic solution yields the analogous *bromiododihydroxypentanthrene* melting at 119° with decomposition. Hydriodic acid reduces the fluorescent

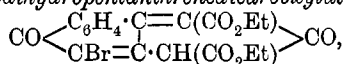
substance to *bromodihydroxypentanthrene*, $OH \cdot C \leq \begin{matrix} C_6H_4 \cdot C \cdot CH \\ CBr - C \cdot CH_2 \end{matrix} > C \cdot OH$,

which crystallises from alcohol in colourless needles and melts and decomposes at 192° ; it is also formed by reduction with zinc dust in alcoholic or glacial acetic acid solution, and, on acetylation, yields *bromodiaceoxypentanthrene*, which crystallises from alcohol and melts at 159° . With hydroxylamine, however, its behaviour is that of its

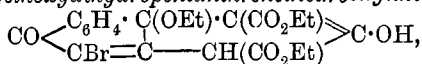
tautomeric form, and the *oxime*, $OH \cdot N : C \leq \begin{matrix} C_6H_4 \cdot CH \cdot CH \\ CBr = C - CH_2 \end{matrix} > C \cdot OH$ or

$OH \cdot C \leq \begin{matrix} C_6H_4 \cdot C \cdot CH_2 \\ CBr - C \cdot CH_2 \end{matrix} > C : N \cdot OH$, is obtained; it crystallises from alcohol in yellowish needles.

Ethyl bromodiketodihydropentanthrenedicarboxylate,

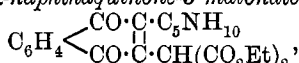


obtained by the action of 3:4-dibromo- β -naphthaquinone on diethyl acetonedicarboxylate (compare Michel, Abstr., 1900, i, 669), crystallises from alcohol in small, yellowish needles, melts at 157° , and is not fluorescent in alkaline solution; it is also not acted on by alcohol and sulphuric acid, or by hydrochloric or hydrobromic acids, but combines additively with alcohol in presence of sodium ethoxide to form *ethyl bromoketohydroxyethoxydihydropentanthrenedicarboxylate*,



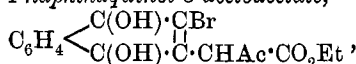
which crystallises from alcohol in needles, melts at $135-137^\circ$, and is not fluorescent. Using *isobutyl* alcohol, the analogous *isobutyl* derivative, $\text{C}_{23}\text{H}_{25}\text{O}_7\text{Br}$, is formed; it crystallises from dilute acetic acid and melts at $142-144^\circ$.

Ethyl 2-piperidino- α -naphthaquinone-3-malonate,



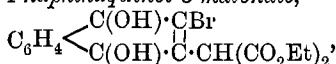
prepared by the interaction of 2-bromo- α -naphthaquinone-3-malonate with piperidine in alcoholic solution, crystallises from alcohol, on adding water, in red needles and melts at 99° .

Ethyl 2-bromo-1:4-naphthaquinol-3-acetoacetate,



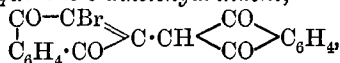
prepared by reducing the corresponding naphthaquinone derivative with zinc dust in glacial acetic acid solution, forms colourless crystals and melts and decomposes at 125° .

Ethyl 2-bromo-1:4-naphthaquinol-3-malonate,



forms colourless needles and melts and decomposes at 130° .

2-Bromo- α -naphthaquinone-3-diketohydrindene,



obtained by heating 2:3-dibromo- α -naphthaquinone with ethyl sodio-diketohydrindenecarboxylate in alcoholic solution at 150° , forms yellow needles and melts at 278° .
W. A. D.

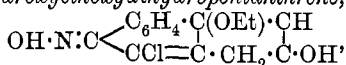
The Fluorescent Compound derived from Ethyl 2-Chloro- α -naphthaquinone-3-acetoacetate. By ALFRED BERTHEIM (*Ber.*, 1901, 34, 1554—1558. Compare preceding abstract).—*Chlorotrihydroxypentanthrene*, $\text{OH} \cdot \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CH} \\ \text{CCl} - \text{C} : \text{CH} \cdot \text{C} \cdot \text{OH} \end{array}$, obtained by the action

of alkali on 2-chloro- α -naphthaquinone-3-acetoacetate (Michel, Abstr., 1900, i, 669), forms yellow leaflets, melts and decomposes at 140° , and is strongly fluorescent in alkaline solution; the following compounds were prepared in the same way as the analogous bromo-derivatives.

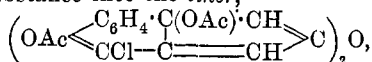
Chlorodihydroxyethoxypentanthrene, $\text{OH} \cdot \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}(\text{OEt}) \cdot \text{CH} \\ \text{CCl} - \text{C} : \text{CH} \cdot \text{C} \cdot \text{OH} \end{array}$, crystallises from benzene in amber-yellow plates and melts at $175-176^\circ$;

chlorodihydroxymethoxypentanthrene separates from benzene as a yellow, crystalline powder and melts at 162—164°; the analogous *isobutyl ether* forms leaflets and melts at 140—141°. *Chlorodiacetoxyethoxypentanthrene* crystallises from alcohol in small, amber coloured plates and melts at 152—153.5°; *chlorodiacetoxibutoxypentanthrene* separates from dilute acetone as a white, crystalline powder and melts at 149°.

Chloroketoximohydroxyethoxydihdropentanthrene,



crystallises from dilute alcohol in bright yellow needles which, when heated, decompose before melting. Acetic anhydride at 55° converts the fluorescent substance into the *ether*,



which can be purified by precipitation with light petroleum from its benzene or chloroform solution.

Dichlorodihydroxypentanthrene, $\text{OH}\cdot\text{C} \begin{array}{l} \text{C}_6\text{H}_4\cdot\text{CCl}\cdot\text{CH} \\ \text{CCl}-\text{C}=\text{CH} \end{array} \text{C}\cdot\text{OH}$,

crystallises from a mixture of benzene and light petroleum in feebly yellow needles and melts and decomposes at 180°. *Chlorobromodihydroxy-*

pentanthrene, $\text{OH}\cdot\text{C} \begin{array}{l} \text{C}_6\text{H}_4\cdot\text{CBr}\cdot\text{CH} \\ \text{CCl}-\text{C}=\text{CH} \end{array} \text{C}\cdot\text{OH}$, forms lustrous, yellow needles from benzene and melts and decomposes at 168—170°.

Chlorodihydroxypentanthrene, $\text{OH}\cdot\text{C} \begin{array}{l} \text{C}_6\text{H}_4\cdot\text{C}-\text{CH} \\ \text{CCl}-\text{C}\cdot\text{CH}_2 \end{array} \text{C}\cdot\text{OH}$, crystallises from alcohol in white, felted needles and melts at 185°; its *diacetyl* derivative forms white needles and melts at 152—156°.

W. A. D.

Synthesis of *r*-Leucine. By EMIL ERLÉNMEYER, jun, and JULIUS KUNLIN (*Annalen*, 1901, 316, 145—156. Compare Abstr., 1899, i, 761).—The *anhydride*, $\text{CHPr}^s:\text{C} \begin{array}{l} \text{N}=\text{CPh} \\ \text{CO}-\text{O} \end{array}$, of α -benzoylamino- β -

isopropylacrylic acid, prepared by heating on the water-bath a mixture of mol. proportions of hippuric acid, *isobutaldehyde*, and fused sodium acetate in the presence of acetic anhydride, crystallises from alcohol in colourless needles or plates and melts at 87°; the substance is insoluble in water but dissolves in the ordinary organic solvents. The *acid*, $\text{CHPr}^s:\text{C}(\text{NH}\cdot\text{COPh})\cdot\text{CO}_2\text{H}$, obtained by treating the anhydride successively with sodium hydroxide and hydrochloric acid, crystallises from dilute alcohol in needles melting at 187°. The *silver salt*, $\text{C}_{13}\text{H}_{14}\text{O}_3\text{NaAg}$, is obtained as a white precipitate; the *barium* and *calcium* salts crystallise in colourless needles. When heated with excess of concentrated ammonia solution in sealed tubes at 150—170°, the preceding acid undergoes hydrolysis, yielding *r*-leucine and benzoic and *isovaleric* acids, the amino-compound being identified by conversion into its copper salt and benzoyl derivative (Fischer, Abstr., 1900, i, 646).

G. T. M.

Dimethyl- and Diethyl-aminobenzoyltetrachlorobenzoic Acids and their Derivatives. By ALBIN HALLER and HERM. UMGROVE (*Bull. Soc. Chim.*, 1901, [iii], 25, 598—603. Compare this vol., i, 276 and 324).—*Dimethylaminobenzoyltetrachlorobenzoic acid*, obtained by the action of dimethylaniline on tetrachlorophthalic anhydride in the presence of aluminium chloride, crystallises in small, yellow scales melting at 211°. The *methyl* and *ethyl* esters, yellow crystalline substances melting at 167° and 143° respectively, cannot be prepared by the ordinary method, but may be obtained by the action of sodium methoxide or ethoxide on the *acetate* or *mixed anhydride*. The latter compound is formed when dimethylaminobenzoyltetrachlorobenzoic acid is heated with dimethylaniline and acetic anhydride, a reaction which was expected to give rise to a phthalein such as is yielded by the non-chlorinated dialkylaminobenzoylbenzoic acids (this vol., i, 325). *Dimethylaminobenzoyltetrachlorobenzoic acid*, obtained by reducing the corresponding benzoyl derivative with zinc and hydrochloric acid, crystallises in slender, white needles melting at 215°. *Diethylaminobenzoyltetrachlorobenzoic acid*, obtained in a similar manner to the corresponding methyl derivative, forms yellow crystals melting at 222°. The *methyl* and *ethyl* esters are yellow, crystalline compounds melting at 160° and 135° respectively, whilst the *acetate* or *mixed anhydride* crystallises in colourless scales melting at 175°. *Diethylaminobenzoyltetrachlorobenzoic acid* forms white crystals melting at 148°. N. L.

Nitrilphenols. By EDMOND FIQUET (*Bull. Soc. Chim.*, 1901, [iii], 25, 591—598).—The action of cyanoacetic acid on *m*- and *p*-hydroxybenzaldehydes in presence of acetic acid results in the formation of cyano-*m*- and *p*-hydroxycinnamic acids. These acids form two series of salts, since they contain both phenolic and carboxylic hydroxyl, are oxidised to picric acid by the action of nitric acid, and lose carbon dioxide when heated under diminished pressure, with the production of *nitriles*. That from the *meta*-acid melts at 148°, whilst that from the *para*-acid is a liquid which partially decomposes on distillation. In the preparation of cyano-*o*-hydroxycinnamic acid, an ester or the sodium salt of cyanoacetic acid must be employed, otherwise an internal anhydride is formed by the interaction of the phenolic and carboxylic hydroxyls.

These nitriles, containing both phenolic hydroxyl and a cyanogen group, were prepared in large quantities for physiological investigation. Nitriles in general are toxic, and the effect of phenolic hydroxyl is usually to increase the toxicity of a compound, phenol, for example, being more toxic than benzene, and salicylic acid than benzoic acid. Nevertheless, the toxicity of nitriles is found to disappear on the introduction of phenolic hydroxyl, the cyanogen and phenol groups being apparently antagonistic as regards their physiological action. It is pointed out that proteid substances behave in many respects like complex nitriles, and that peptones may be compared with nitrilphenols, the non-toxicity of which is due to a state of physiological equilibrium. It would seem also that the introduction of phenols into the organism

not only prevents the development of micro-organisms, but neutralises the toxicity of the products secreted by them. N. L.

Preparation of the Esters of *o*-, *m*-, and *p*-Nitrobenzoylcyanacetic Acid and Crystallised *o*-Nitrobenzoic Chloride. By MAVROJANNIS (*Compt. rend.*, 1901, 132, 1054—1055).—Substituted benzoyl derivatives of ethyl cyanoacetate are produced by treating the sodium derivative of this ester dissolved in alcohol with an ethereal solution of the corresponding acid chloride.

Ethyl o-nitrobenzoylcyanacetate, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$, obtained by the use of *o*-nitrobenzoic chloride, separates from ether in prismatic crystals melting at 89° ; it is almost insoluble in water but readily dissolves in the ordinary organic solvents. *o*-Nitrobenzoic chloride, when freed from phosphorus oxychloride by distillation under 50 mm. pressure, slowly solidifies and separates from its solution in light petroleum in colourless crystals melting at 24 — 25° .

Ethyl m-nitrobenzoylcyanacetate crystallises from alcohol in silky needles and melts at 110° ; its *para*-isomeride also separates in white needles melting at 158° ; these esters are almost insoluble in water and dissolve but sparingly in the ordinary organic solvents.

G. T. M.

Derivatives of Anthranilic Acid. By HANS MEHNER (*J. pr. Chem.*, 1901, [ii], 63, 241—312).—By the action of formaldehyde on anthranilic acid in acid solution, a yellow, amorphous substance is obtained.

Methyl methylenedi-o-aminodibenzoate, $\text{CH}_2(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me})_2$, formed when formaldehyde condenses with methyl *o*-aminobenzoate without a condensing agent, crystallises in needles melting at 119 — 120° and boils and partially decomposes at 280° ; its solution exhibits an intense blue fluorescence. On heating with ammonia, it yields hexamethylenetetramine; by acids, it is decomposed into formaldehyde and methyl *o*-aminobenzoate.

Methyl-4 : 4'-diaminodiphenylmethane-3 : 3'-dicarboxylate,
 $\text{CH}_2[\text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CO}_2\text{Me}]_2$,

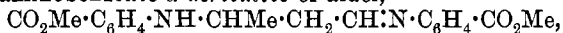
produced by isomeric change from the last-mentioned compound by warming with hydrochloric acid, crystallises in white plates melting at 147° , and forms a *dihydrochloride*, a *diacetyl* derivative, which crystallises in lustrous plates melting at 161 — 163° , and a *dibenzoyl* derivative forming needles which melt at 221.5° .

On treating the diazonium derivative of the base with aniline hydrochloride, a mixture of a mono- and a di-diazoamino-compound is obtained. The *oxyazo*-derivative of the base and β -naphthol, $\text{CH}_2[\text{C}_6\text{H}_3(\text{CO}_2\text{Me}) \cdot \text{N}_2\text{H} \cdot \text{C}_{10}\text{H}_6\text{O}]_2$, forms small, dark-red crystals; the compound with phenol, $\text{CH}_2[\text{C}_6\text{H}_3(\text{CO}_2\text{Me}) \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}]_2$, was obtained as a dark-red powder.

4 : 4'-Diaminodiphenylmethane-3 : 3'-dicarboxylic acid, prepared from the ester, forms yellowish needles which melt at 239° ; the salts are all unstable. The *monomethyl* ester is produced by boiling methyl methylenediaminodibenzoate with hydrochloric acid for 1 hour, when

isomerisation and partial hydrolysis take place, crystallises in needles melting at 178—179°, and forms a *silver salt*, $C_{16}H_{15}O_4N_2Ag$.

Methyl ethyldenedi-o-aminodibenzoate, $CHMe(NH \cdot C_6H_4 \cdot CO_2Me)_2$, prepared by the action of acetaldehyde on methyl *o*-aminobenzoate in ethereal solution, crystallises in large, colourless crystals melting at 130—131°; in solution, it exhibits a blue fluorescence, and is decomposed by acids. Transformation into a diphenylethane could not be effected. Attempts to benzoylate it led to the production of *methyl o-benzoylaminobenzoate*, $NHBz \cdot C_6H_4 \cdot CO_2Me$, which crystallises in needles melting at 100°. In acid solution, acetaldehyde forms with methyl *o*-aminobenzoate a *derivative of aldol*,



which forms colourless crystals melting at 146°.

Derivatives of methyl diazoaminobenzene-2-carboxylate. *Methyl o-diazoaminobenzoate*, $N_3HPh \cdot C_6H_4 \cdot CO_2Me$, prepared by adding aniline hydrochloride to diazotised methyl *o*-aminobenzoate, crystallises in yellow needles melting at 71°. The same diazoamino-compound is obtained when benzenediazonium nitrate and the methyl ester interact in pyridine, but not in aqueous solution. Attempts to transform this compound into the azoamino-compound failed. 3-Phenylphenotriazone and methyl alcohol are formed when the last-mentioned diazoamino-compound is boiled with dilute alcohol; the former is identical with the substance obtained by Pictet and Gonset (*Abstr.*, 1898, i, 213). Heated with concentrated hydrochloric acid, the triazone yields chiefly *o*-chlorobenzoic acid. Reduction with stannous chloride produces anthranilic acid and phenylhydrazine. Alcoholic sodium hydroxide converts it into *sodium o-diazoaminobenzoate*, which crystallises in sulphur-yellow needles.

o-Diazoaminobenzoic acid, $N_3HPh \cdot C_6H_4 \cdot CO_2H$, prepared from the sodium salt, or from anthranilic acid and benzenediazonium chloride, forms unstable, faintly yellow leaves or prisms, melting and decomposing at 121°. The *potassium*, *ammonium*, and *silver* salts are all sparingly soluble in water.

Methyl o-toluenediazoaminobenzoate, $C_6H_4Me \cdot N_3H \cdot C_6H_4 \cdot CO_2Me$, prepared from *o*-toluidine hydrochloride and diazotised methyl *o*-aminobenzoate, crystallises in yellow needles melting at 69.5°. The corresponding *para*-compound forms straw-yellow needles melting at 115.5°, and the *meta*-compound together with *methyl m-toluidineazobenzoate*, $NH_2 \cdot C_6H_2Me \cdot N_2 \cdot C_6H_4 \cdot CO_2Me$, are formed from *m*-toluidine hydrochloride and diazotised methyl *o*-aminobenzoate. The diazoamino-derivative crystallises in yellow needles melting at 87.5°; the azoamino-compound separates in red needles melting at 93°, and is far less soluble in petroleum than the diazoamino-compound.

3-*o-Tolylphenotriazone*, $C_6H_4 \begin{smallmatrix} CO \cdot N \cdot C_6H_4Me \\ \diagup \quad \diagdown \\ N=N \end{smallmatrix}$, obtained from the corresponding diazoamino-compound, forms small, colourless needles melting at 166°. 3-*p-Tolylphenotriazone* crystallises in small needles or prisms melting at 143°, and 3-*m-tolylphenotriazone* in needles melting at 150°. These three substances are obtainable respectively from the three *o*-aminobenzoyltoluidides.

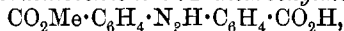
Methyl m-xylenediazoaminobenzoate, $C_6H_3Me_2 \cdot N_3H \cdot C_6H_4 \cdot CO_2Me$,

crystallises in yellow needles melting at 85° . 3-*m-Xylylphenotriazone*, prepared from the latter, crystallises in white needles melting at 132° .

o-Aminobenzoyl o-toluidide, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{Me}$, prepared by heating isatoic anhydride with *o*-toluidine (compare Kolbe, Abstr., 1885, 58), crystallises in white needles melting at 104° . The *p*-toluidide forms needles melting at 151° , the *m*-toluidide needles melting at 118° , and the *m*-xylylidide needles melting at 138° . By the action of sodium nitrite in acid solution, these compounds are converted into the triazones already described.

Methyl m-nitro-o-diazoaminobenzoate, prepared from *m*-nitroaniline and methyl *o*-diazobenzoate, forms yellow needles melting at 167° . 3-*m-Nitrophenylphenotriazone* crystallises in white needles melting at 238° . *Methyl p-nitro o-diazoaminobenzoate* crystallises in golden-yellow needles melting at 184° , and is converted into 3-*p-nitrophenylphenotriazone*, which crystallises in colourless needles melting at 252 – 254° . Both these nitro-esters are converted with ease into the triazones, and in this respect contrast with the corresponding methyl derivatives previously described. In no circumstances could a condensation be effected between *o*-nitroaniline and methyl *o*-diazobenzoate.

Monomethyl diazoaminobenzene-2 : 2'-dicarboxylate,

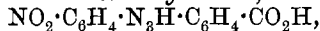


prepared from methyl *o*-diazobenzoate and anthranilic acid, crystallises in small needles, which melt and decompose at 127° and could not be converted into a triazone.

With *m*-phenylenediamine, methyl *o*-diazobenzoate yields the *hydrochloride* of *methyl chrysoidine-2-carboxylate*, $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_4 \cdot \text{HCl} \cdot \text{H}_2\text{O}$, which forms violet-red needles; the *base*, $\text{C}_6\text{H}_8(\text{NH}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, crystallises in brownish-red leaves which melt at 138° . The diazoamino-compound could not be obtained.

m-Toluenediazoaminobenzoic acid, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_3\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, is obtained by the action of *m*-toluenediazonium salts on anthranilic acid, and not by the action of *o*-diazobenzoic acid on *m*-toluidine except in pyridine solution; it forms pale yellow plates melting and decomposing at 114° . The *p*-toluene compound crystallises in pale yellow leaves, melting and decomposing at 118° . Neither diazotised *o*-toluidine nor *m*-xylylidine could be induced to combine with anthranilic acid; the presence of the methyl group in the ortho-position appears to prevent the condensation.

o-Nitrodiazoaminobenzene-2-carboxylic acid,



prepared from *o*-nitrobenzenediazonium salts and anthranilic acid, forms small, golden-yellow needles melting and decomposing at 140° ; the *m*-nitro-derivative crystallises in pale yellow needles melting and decomposing at 166.5° , the *p*-nitro-derivative in small, yellow needles melting and decomposing at 171° . None of these acids could be converted into a triazone. They can, however, all be obtained by boiling the triazones with alcoholic sodium hydroxide or by hydrolysing the corresponding methyl esters.

o-Toluenediazoaminobenzoic acid, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_3\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, obtained from the triazone previously described, forms pale yellow leaflets, melting and decomposing at 95 – 96° .

m-Xylenediazoaminobenzoic acid, easily prepared from the corresponding triazone, crystallises in pale yellow leaflets melting and decomposing at 117°.

A convenient and simple apparatus for measuring the nitrogen given off from a diazoamino-compound under the action of an acid is described; it is a modification of that devised by Goldschmidt and Reinders (Abstr., 1896, ii, 515), and is found to give accurate results. By its means, the relative proportion of diazoamino- and aminoazo-derivatives, formed from methyl *o*-diazobenzoate and the hydrochlorides of various aromatic bases, have been determined. Aniline yields 92.2 per cent. of diazoamino-compound, *o*-toluidine 93.0, *m*-toluidine 64.24, *p*-toluidine 98.53, and *m*-xylydine 95.2 per cent. K. J. P. O.

Esters of Phloroglucinolcarboxylic Acids. By JOSEF HERZIG and FRANZ WENZEL [and, in part, PAUL ALTMANN] (*Monatsh.*, 1901, 22, 215—231. Compare Abstr., 1900, i, 176).—The method of preparing methyl phloroglucinolcarboxylate previously given (*loc. cit.*) from methyl iodide and silver phloroglucinolcarboxylate is found to yield, not only the above ester (m. p. 170—172°), but also methyl dimethylphloroglucinolcarboxylate and phloroglucinolcarboxylic acid; the quantity of the latter largely preponderates.

Methyl dimethylphloroglucinolcarboxylate, $C_6Me_2(OH)_3 \cdot CO_2Me$, crystallises from dilute alcohol in white needles melting at 138—140°. The *monoacetate*, prepared by boiling the ester for $\frac{1}{2}$ hour with acetic anhydride, melts at 98—101°; the *triacetate*, formed only in the presence of sodium acetate, melts at 124—126°.

By the action of acetic anhydride on methyl phloroglucinolcarboxylate, a *diacetate* is obtained melting at 83—86°; whilst in the presence of sodium acetate the *triacetate* is formed, melting at 77—79°.

Methoxyphloroglucinolcarboxylic acid, $OMe \cdot C_6H_2(OH)_2 \cdot CO_2H$, prepared as the sodium salt by heating the sodium derivative of methoxyphloroglucinol with carbon dioxide under a pressure of 5 atmospheres, crystallises in grey needles melting and decomposing at 141°.

Methyl methoxyphloroglucinolcarboxylate cannot be prepared by the usual methods, but is readily obtained by treating the acid in ethereal solution with diazomethane. It forms colourless needles, melting at 114—116°. With alcoholic potash, the ester yields only methoxyphloroglucinol. It is, however, easily converted into the acid by heating with concentrated sulphuric acid at 90—95° for 10 minutes.

K. J. P. O.

Some Derivatives of Dibromothymoquinone. By J. HOFFMANN (*Ber.*, 1901, 34, 1558—1561).—*Ethyl bromothymoquinonemalonate*, $CB\text{r} \begin{array}{c} \text{CPr}^{\beta}-\text{CO} \\ \text{CO}-\text{CMe}^{\beta} \end{array} \rangle \text{C} \cdot \text{CH}(\text{CO}_2\text{Et})_2$, obtained by the action of ethyl sodiomalonate on dibromothymoquinone suspended in alcohol, crystallises in yellow needles and melts at 78°; the *barium* salt is an amorphous blue powder. The action of either ethyl cyanoacetate or ethyl acetoacetate on dibromothymoquinone yields only oily products.

When *p*-toluidine is boiled with dibromothymoquinone in alcoholic solution, a methyl group, not a bromine atom, is replaced, 2-*p*-toluidino-

3:6-dibromo-5-isopropyl-1:4-benzoquinone being formed; it crystallises from alcohol in dark violet needles and melts at 195° . 3:6-Dibromo-2-anilino-5-isopropyl-1:4-benzoquinone, obtained by using aniline, crystallises from alcohol in dark blue needles and melts at 170° ; Carstanjen (this Journal, 1871, 350) has stated, without analysing his product, that this action yields a dianilinothymoquinone. The structure of the anilide and toluidide follows from their both yielding 3:6-dibromo-2-hydroxy-5-isopropyl-1:4-benzoquinone when boiled with 20 per cent. alcoholic sulphuric acid for 2—3 hours; this crystallises from light petroleum in reddish-brown needles, melts at 143° and yields a silver derivative, which separates from alcohol in red needles. The latter with methyl iodide gives 3:5-dibromo-2-methoxy-5-isopropyl-1:4-benzoquinone, which crystallises from methyl alcohol in yellow leaflets and melts at $62-63^{\circ}$; the analogous ethoxy-derivative crystallises from ethyl alcohol in golden leaflets and melts at $59-60^{\circ}$. W. A. D.

Friedel and Crafts' Reaction. By J. BOESEKEN (*Rec. Trav. Chim.*, 1901, 20, 102—106).—In support of views previously stated (Abstr., 1900, i, 349; compare Perrier, *ibid.*, 331), it is shown that acetyl chloride combines with aluminium chloride in carbon disulphide solution at -10° , giving the additive compound, $\text{AcCl} \cdot \text{AlCl}_3$; it is a non-crystallisable, yellowish syrup, which interacts with benzene in carbon disulphide solution to form the compound, $\text{COPhMe} \cdot \text{AlCl}_3$, melting at 64° . This, when decomposed by water, yields acetophenone; in like manner, acetyltoluene and acetylxylylene were prepared.

Contrary to Combe's statement (*Ann. Chim. Phys.*, 1887, [vi], 12, 199), when the product resulting from the complete condensation of acetyl chloride with aluminium chloride to form $\text{CH}_3\text{Ac} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COCl}$, is boiled with benzene, no acetophenone is formed; the latter is only obtained in cases where some of the acetyl chloride has remained unacted on. W. A. D.

Disulphones. VI. Sulphonal Derivatives of Unsaturated Ketones. By THEODOR POSNER (*Ber.*, 1901, 34, 1395—1405).—Substances such as mesityl oxide, $\text{CMe}_2 \cdot \text{CH} \cdot \text{CO} \cdot \text{CH}_3$, benzylideneacetone, $\text{CHPh} \cdot \text{CH} \cdot \text{CO} \cdot \text{CH}_3$, benzylideneacetophenone, $\text{CHPh} \cdot \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$, and dypnone, $\text{CMePh} \cdot \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$, which contain a ketonic carbonyl group and one neighbouring double bond, condense with 3 mols. of ethyl hydrosulphide when the mixture of unsaturated ketone and hydrosulphide is saturated with dry gaseous hydrogen chloride; the grouping $\text{C} \cdot \text{CH} \cdot \text{CO}$ becomes $\text{CH} \cdot \text{CH}(\text{SEt}) \cdot \text{C}(\text{SEt})_2$. On the other hand, when there are two double bonds adjoining the ketonic carbonyl, as in phorone, $\text{CO}(\text{CH} \cdot \text{CMe}_2)_2$, and dibenzylideneacetone, $\text{CO}(\text{CH} \cdot \text{CHPh})_2$, the substance reacts with 2 mols. only of the hydrosulphide, and not with 4; only the carbonyl reacts, the grouping $\text{CO}(\text{CH} \cdot \text{C})_2$ becoming $\text{C}(\text{SEt})_2(\text{CH} \cdot \text{C})_2$. Cold aqueous potassium permanganate oxidises these thioethyl compounds (mercaptols) respectively to trisulphones with the grouping $\text{CH} \cdot \text{CH}(\text{SO}_2\text{Et}) \cdot \text{C}(\text{SO}_2\text{Et})_2$, or disulphones with $\text{C}(\text{SO}_2\text{Et})_2(\text{CH} \cdot \text{C})_2$. In the case of benzylideneacetone, however, the main product of the oxidation is not a trisulphone, but a ketomono-sulphone with the grouping $\text{CH} \cdot \text{CH}(\text{SO}_2\text{Et}) \cdot \text{CO}$; this is less soluble in alcohol than the normal product, which is formed also, although in

small amount. The trisulphones do not react with bromine, as indeed might be expected; the disulphones, however, which still contain (two) double bonds, do react slowly; hydrogen bromide is eliminated, and the product is a bromo-substitution derivative, dibromo- in the case of the phorone compound, monobromo- in the case of dibenzylideneacetone. Presumably the primary product in each case was an additive product, with 4Br and 2Br respectively.

The compounds described are enumerated below with their melting points; the thioethyl compounds (mercaptols) were obtained as oils, and were not analysed. From mesityl oxide: $\gamma\delta\delta$ -Trithioethyl- β -methylpentane (mesityl oxide sesquimercaptol); $\gamma\delta\delta$ -triethylsulpho- β -methylpentane (mesityl oxide trisulphone), 100°. From phorone: δ -Dithioethyl- $\beta\zeta$ -dimethylhepta- $\beta\epsilon$ -diene (phorone mercaptol); δ -diethylsulpho- $\beta\zeta$ -dimethylhepta- $\beta\epsilon$ -diene (phorone disulphone), 101°, dibromo-derivative, 139—140°. From benzylideneacetone: $\beta\beta\gamma$ -Trithioethyl- δ -phenylbutane (benzylideneacetone sesquimercaptol); $\beta\beta\gamma$ -triethylsulpho- δ -phenylbutane (benzylideneacetone trisulphone), 154°. From dibenzylideneacetone: γ -Dithioethylsulpho- $\alpha\epsilon$ -diphenylpenta- $\alpha\gamma$ -diene (dibenzylideneacetone mercaptol); γ -diethylsulpho- $\alpha\epsilon$ -diphenylpenta- $\alpha\gamma$ -diene (dibenzylideneacetone disulphone), 140—142°, monobromo-derivative, 173°. From benzylideneacetophenone: $\alpha\alpha\beta$ -Trithioethyl- $\alpha\gamma$ -diphenylpropane (benzylideneacetophenone sesquimercaptol); β -ethylsulpho- $\alpha\gamma$ -diphenylpropan- α -al (benzylideneacetophenone ketomonosulphone), 156°; $\alpha\alpha\beta$ -triethylsulpho- $\alpha\gamma$ -diphenylpropane (benzylideneacetophenone trisulphone), 125°. From dypnone: $\alpha\alpha\beta$ -Trithioethyl- $\alpha\gamma$ -diphenylbutane (dypnone sesquimercaptol); $\alpha\alpha\beta$ -Triethylsulpho- $\alpha\gamma$ -diphenylbutane (dypnone trisulphone), 120—120.5°. C. F. B.

Phenylacetylacetophenone (Phenylacetylbenzoylmethane, Phenacyl Benzyl Ketone). By CARL BÜLOW and HANS GROTHOWSKY (*Ber.*, 1901, 34, 1479—1488).—*Phenylacetylacetophenone*, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COPh}$,

prepared by the action of sodium on a mixture of ethyl phenylacetate and acetophenone in the presence of ether, crystallises in colourless prisms, melts at 54—56°, and gives a red coloration with ferric chloride in alcoholic solution. The copper compound, $\text{Cu}(\text{C}_{16}\text{H}_{13}\text{O}_2)_2$, forms greyish-green needles which melt and decompose at 117°. No dioxime or diphenylhydrazone could be obtained, and it appears probable that after the replacement of the oxygen of one carbonyl group, the resulting keto-monoxime or monophenylhydrazone passes into the enolic form, and then loses water. 3 (or 5)-Phenyl-5 (or 3)-benzylisooxazole, $\text{C}_{16}\text{H}_{13}\text{ON}$, is formed by the action of hydroxylamine hydrochloride on the diketone and crystallises in colourless prisms melting at 92°. 1 : 3 (or 5)-Diphenyl-5 (or 3)-benzylpyrazole, $\text{C}_{22}\text{H}_{18}\text{N}_2$, is obtained by the action of phenylhydrazine on the diketone, and crystallises in fascicular groups of needles melting at 76°. The diketone also reacts with semicarbazide, forming 5 (or 3)-phenyl-3 (or 5)-benzylpyrazole, $\text{C}_{16}\text{H}_{14}\text{N}_2$, which crystallises in colourless needles melting at 90.5—91°. *Benzeneazophenylacetylacetophenone*, $\text{COPh}\cdot\text{CH}(\text{N}_2\text{Ph})\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, is formed by the action of benzenediazonium chloride on the diketone, and

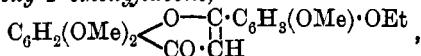
crystallises in yellow, lustrous needles melting at 119—120°. When heated with a large excess of phenylhydrazine, it yields 4-*benzeneazo*-1:3 (or 5)-*diphenyl*-5 (or 3)-*benzylpyrazole*, $C_{28}H_{22}N_4$, which crystallises in orange-red, lustrous needles melting at 150°, and can be distilled almost without decomposition. *isoNitrosophenylacetylacetophenone*, $COPh \cdot C(:N \cdot OH) \cdot CO \cdot CH_2Ph$, formed by the action of amyl nitrite and hydrochloric acid on the diketone, crystallises in colourless needles which melt and decompose at 131°. It was found impossible to obtain a triketone by hydrolysis of this compound, dilute acids and alkalis, and even alcohol, yielding on boiling hydrogen cyanide, phenylacetic acid, and benzoic acid. *isoNitrosophenylacetylacetophenonemonosemicarbazone*, forms colourless crystals and decomposes at about 220°. The corresponding *monoxime* crystallises in colourless prisms and melts and decomposes at 167°. A. H.

Synthesis of Luteolin. By E. DILLER and STANISLAUS VON KOSTANECKI (*Ber.*, 1901, 34, 1449—1453).—2:4:6:3':4'-Penta-methoxybenzoylacetophenone, $C_6H_2(OMe)_3 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_3(OMe)_2$ (this vol., i, 92), prepared by a slightly modified method, has been obtained in a crystalline form, separates from alcohol in small, nodular aggregates or crystalline crusts, and melts at 112—113.5°.

2:4:6:3'-Tetramethoxy-4'-ethoxybenzoylacetophenone, $C_6H_2(OMe)_3 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_3(OMe) \cdot OEt$, separates from alcohol in crystalline crusts consisting of minute needles and melts at 106—107°. The *isonitroso*-derivative, $C_{21}H_{23}NO_8$, prepared by the action of amyl nitrite and hydrochloric acid on a solution in chloroform of the diketone, crystallises from a mixture of acetic acid and alcohol in short, stout, yellow needles and melts at 170° with liberation of gas.

isoNitroso-2:4:6:4'-tetramethoxybenzoylacetophenone, $C_6H_2(OMe)_3 \cdot CO \cdot C(:NOH) \cdot CO \cdot C_6H_4 \cdot OMe$, crystallises from a mixture of acetic acid and alcohol in yellow prisms and melts at 189° with liberation of gas.

5:7:3'-Trimethoxy-4'-ethoxyflavone,



prepared by adding the tetramethoxyethoxyacetophenone to warm hydriodic acid of sp. gr. 1.7, crystallises from xylene in white needles and melts at 222—222.5°; it is only slowly converted into luteolin by heating with hydriodic acid of sp. gr. 1.9, and the luteolin, which crystallises in needles, is mixed with a *luteolin methyl ether*, $C_{16}H_{16}O_6$, crystallising in flakes (compare Perkin and Horsfall, *Trans.*, 1900, 77, 1320), which melts at 270° and is probably 7-methoxy-5:3':4'-tri-hydroxyflavone, for Perkin appears to have obtained it also from luteolin-7:3':4'-trimethyl ether.

Fleischer's digitoflavone (*Abstr.*, 1899, i, 631) very closely resembles luteolin and is perhaps identical with it. T. M. L.

Isomeric Bromodiphenacyls. By CARL PAAL and HERM. STERN (*Ber.*, 1901, 34, 1609—1613. Compare Fritz, *Abstr.*, 1896, i, 151; Paal and Demeler, *ibid.*, 687).—The two isomeric bromodiphenacyls

readily form additive compounds with acid chlorides. The derivatives from the bromodiphenacyl melting at 129° are termed α - and the isomeric substances β -compounds. They are readily formed when the constituents are gently warmed together, best in sealed tubes at 100° or 110° . The following compounds are described :

| | α -Bromodiphenacyl. | β -Bromodiphenacyl. |
|------------------|------------------------------|-----------------------------------|
| Acetyl chloride | Needles, m. p. 122° | Prisms, m. p. 91° . |
| Valeryl chloride | „ m. p. 146° | m. p. 101° . |
| Benzoyl chloride | „ m. p. 152° | Needles m. p. $134-135^{\circ}$. |

Most of the compounds crystallise well from alcohol.

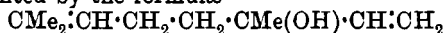
J. J. S.

Constitution of Camphor. By OSSIAN ASCHAN (*Annalen*, 1901, 316, 196—241. Compare Abstr., 1896, i, 492).—This communication, although an important contribution to the chemistry of camphor from the stereochemical standpoint, is not suitable for abstraction. The experimental results described in the paper have already been published (Abstr., 1894, i, 538). The production of inactive camphane by reducing *l*- or *d*-bornyl iodide (*l*- or *d*-pinene hydriodide) is very weighty evidence in favour of Bredt's formula for camphor (Abstr., 1894, i, 422 ; 1900, i, 399).

G. T. M.

Myrcenol and its Constitution. By PHILIPPE BARBIER (*Compt. rend.*, 1901, 132, 1048—1050).—The name *myrcenol* is given to the alcohol obtained by Power and Kléber (Abstr., 1895, ii, 295) on hydrating myrcene, the compound being isomeric and not identical with licareol. Myrcenol is a colourless, oily liquid boiling at $99-101^{\circ}$ under 10 mm. pressure, and slowly undergoing polymerisation ; it has a sp. gr. 0.9012 at 14.5° , and n_D 1.47787 at the same temperature. The molecular refraction as deduced from experiment is 48.35, whilst the theoretical value of the latter constant calculated on the assumption of two double linkings is 48.60. *Myrcenyl acetate*, $C_{10}H_{17}O \cdot Ac$, is a colourless liquid boiling at $111-112^{\circ}$. The boiling points of the alcohol and its acetate are markedly different from the corresponding constants observed in the case of licareol. Myrcenol, when oxidised with a sulphuric acid solution of chromic acid, yields acetone, lævulic acid, and an aldehyde, $C_{10}H_{16}O$, boiling at 110° under 10 mm. pressure. This aldehyde is first isolated in the form of its oxime, $C_{10}H_{17}NO$, which boils at $148-150^{\circ}$ under 10 mm. pressure ; the *semicarbazone*, $C_{10}H_{16} \cdot N \cdot NH \cdot CO \cdot NH_2$, is a crystalline powder melting at $195-196^{\circ}$. When myrcenol is oxidised, first with 1 per cent. permanganate solution and then with chromic acid mixture, it yields only lævulic and succinic acids.

These results indicate that the constitution of myrcenol and myrcene may be represented by the formulæ



and $CMe_2 \cdot CH \cdot CH_2 \cdot \dot{C}H \cdot CMe \cdot \dot{C}H \cdot CH_2$ respectively. The formation of the aldehyde $C_{10}H_{16}O$ results from the oxidation of the terminal methylene group to $\dot{C}H \cdot OH$, and subsequent rearrangement compar-

able with that obtaining among the initial members of the olefine series when these are oxidised to the corresponding aldehydes.

G. T. M.

Dyeing with Oxidic Mordants. By CARL T. LIEBERMANN (*Ber.*, 1901, 34, 1562—1565).—A reply to a misstatement by A. Buntrock (*Rev. gén. matières colorantes*, 1901, 5, 99) of the author's views as to the dyeing properties of anthraquinone derivatives (Liebermann and Kostanecki, *Abstr.*, 1885, 1209; *Annalen*, 1887, 240, 246).

W. A. D.

Brazilin and Hæmatoxylin. Part VI. Brazilein. By JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1901, 22, 207—214. Compare *Abstr.*, 1899, i, 381, 821).—The constitutional formula to be assigned to brazilin is discussed in the light of the recent work of Gilbody and Perkin (*Proc.*, 1899, 15, 27, 75, 241, and 1900, 16, 105), and the view is expressed that the constitution of brazilein offers the key to the solution of the problem.

Although brazilein cannot itself be acetylated, the substance obtained from it by reduction with zinc dust and acetic acid yields a *tetra-acetyl* derivative, $C_{16}H_8(OAc)_4$, which crystallises in white plates from acetic acid, melting at 210—211°. All attempts to remove the acetyl groups failed. On hydrolysis with alkalis, a red solution is obtained, resembling alkaline solutions of brazilein. In the reduction, the fifth oxygen atom of brazilein, $C_{16}H_{12}O_5$, which is not hydroxylic, has been entirely removed, and only the four hydroxylic oxygen atoms remain.

K. J. P. O.

Preparation and composition of the Digitalis Glucosides. By MAX CLOETTA (*Chem. Centr.*, 1901, i, 1102—1103; from *Arch. exp. Path. Pharm.*, 1901, 45, 435—446).—Crystalline and amorphous digitonin are both precipitated by adding ether to a solution of "digitalinum germanicum" in 90 per cent. alcohol, but when the mixture is dissolved in water, alcohol added, and the solution shaken with ether, crystals separate from the ethereal extract after a time, and by repeating the process, a pure crystallised digitonin, $C_{28}H_{47}O_{14} + H_2O$, may be isolated. It is easily soluble in hot water or alcohol, and with warm concentrated hydrochloric acid forms a yellow solution which quickly becomes green. Its solutions give a precipitate with tannic acid, lead acetate, and ammonia, but not with magnesium sulphate and ammonium sulphate. The anhydrous compound is prepared by adding absolute alcohol to a solution of the hydrate in 96 per cent. alcohol. The leaves of *Digitalis* also contain an extremely small quantity of crystalline digitonin.

Amorphous digitonin, $C_{27}H_{46}O_{14}$, prepared from the mother liquor of the preceding compound, is a very hygroscopic white powder, is readily soluble in water, and on warming with concentrated hydrochloric acid forms a red coloration. Unlike crystalline digitonin, the amorphous compound gives Keller's reaction, and its solutions also form a precipitate, not only with tannic acid, lead acetate, and ammonia, but also with magnesium sulphate and ammonium sulphate. Schmiedeberg's

amorphous, and Kiliani's crystalline, digitonin must therefore be different compounds.

Amorphous digitonin is contained in both the leaves and seeds of *Digitalis purpurea*; digitoxin has also been found in the seeds. Attempts to isolate "digitalinum verum" from the leaves were not successful.

E. W. W.

An Isomeride of Apigenin. By STANISLAUS VON KOSTANECKI and FRANZ WEBEL (*Ber.*, 1901, 34, 1454—1457).—Ethyl *o*-ethoxybenzoate condenses with *s*-trimethoxyacetophenone in presence of metallic sodium to form 2:4:6-trimethoxy-2'-ethoxybenzoylacetophenone, $C_6H_2(OMe)_3 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot OEt$, which crystallises from alcohol in long, striated prisms and melts at 112° . By heating with hydriodic acid, it is converted into 5:7:2'-trihydroxyflavone, $C_6H_2(OH)_2 \begin{matrix} O-C_6H_4-OH \\ | \\ CO \cdot CH \end{matrix}$,

which crystallises from acetic acid in pale yellow needles, and melts at 281° ; the triacetyl derivative, $C_{21}H_{16}O_8$, crystallises from alcohol in white, silky needles and melts at 178° . 5-Hydroxy-7:2'-dimethoxyflavone, $C_{15}H_{10}O_2(OMe)_2 \cdot OH$, prepared by the action of methyl iodide and potassium hydroxide on an alcoholic solution of the trihydroxyflavone, crystallises from alcohol in groups of pale yellow needles, melts at 154 — 156° , and gives a sparingly soluble, yellow sodium salt; the acetyl derivative, $C_{15}H_7O_2(OMe)_2 \cdot OAc$, crystallises from dilute alcohol in white needles and melts at 96 — 97° . 5-Hydroxy-7:2'-diethoxyflavone, $C_{15}H_7O_2(OEt)_2 \cdot OH$, crystallises from alcohol in pale yellow needles and melts at 108 — 110° ; the acetyl derivative, $C_{15}H_7O_2(OEt)_2 \cdot OAc$, crystallises from dilute alcohol in white needles and melts at 120 — 122° .

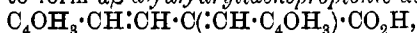
5:7-Dimethoxy-2'-ethoxyflavone, $C_{15}H_7O_2(OMe)_2 \cdot OEt$, prepared by cautiously heating trimethoxyethoxybenzoylacetophenone with hydriodic acid, crystallises from alcohol in white needles and melts at 164 — 165° .

T. M. L.

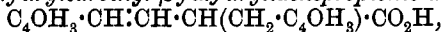
Condensation Products of Furfuraldehyde with Succinic Acid. By FRITZ FICHTER and BEDA SCHEUERMANN (*Ber.*, 1901, 34, 1626—1632).—In the presence of sodium ethoxide, furfuraldehyde and ethyl succinate condense to form furfurylidenesuccinic and difurfurylidenesuccinic acids, together with furfuryl alcohol and pyromucic acid. Furfurylidenesuccinic acid, $CO_2H \cdot C(CH_2 \cdot C_4OH_3) \cdot CH_2 \cdot CO_2H$, crystallises from water in long, yellowish needles decomposing at 205 — 215° . The barium, $C_9H_6O_5Ba \cdot H_2O$, calcium, with H_2O , and silver salts all form needles. On reduction with sodium amalgam, furfurylcarbonylsuccinic acid is obtained (*Abstr.*, 1900, i, 306). Difurfurylidenesuccinic acid, $C_{14}H_{10}O_6$, is much less soluble in water than the preceding acid, and crystallises in short prisms decomposing at 217 — 225° ; the barium salt, with $3H_2O$, crystallises in compact prisms; the calcium salt, with $2H_2O$, in aggregates of needles, and the anhydrous silver salt in microscopic plates. On reduction with sodium amalgam, difurfuryldicarbonylsuccinic acid, $C_{14}H_{14}O_6$, is obtained as white crystals melting at 173° .

Furfuraldehyde condenses with sodium succinate in the presence of

acetic anhydride to form $\alpha\beta$ -difurfurylidenepropionic acid,



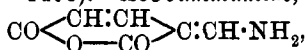
which forms yellow needles melting and decomposing at $195-197^\circ$, and is a very feeble acid. The barium salt, with $6\text{H}_2\text{O}$, forms flattened needles or plates; the magnesium salt, with $8\text{H}_2\text{O}$, small plates. On reduction, α -furfurylcarbonyl- β -furfurylidenepropionic acid,



is obtained, and crystallises in small, white needles melting at $66-67^\circ$.

K. J. P. O.

isoCoumalic Acid. By HANS VON PECHMANN [with MAX HAUSER] (*Ber.*, 1901, 34, 1406-1408).—*isoCoumalamide*, probably



is obtained by the prolonged action of ammonia on methyl coumalate; it has a reddish tinge, melts and decomposes at $230-234^\circ$, and is insoluble in cold, aqueous sodium carbonate. When boiled with aqueous potassium carbonate, it forms the potassium salt of *iso-coumalic acid*; this acid, probably $\text{CO} \begin{array}{c} \text{CH}:\text{CH} \\ \text{O} \quad \text{CO} \end{array} \text{C}:\text{CH}\cdot\text{OH}$, melts and decomposes at $170-180^\circ$, is a monobasic acid, gives a violet-red coloration with ferric chloride even in benzene solution, and reacts with methyl alcohol at the ordinary temperature to form a methyl ester.

C. F. B.

Action of Ethyl Iodide on Caffeine. By A. I. ROSSOLIMO (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 247-249. Compare this vol., i, 161).—*Caffeine ethobromide*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\cdot\text{EtBr}$, prepared by the action of silver bromide on the ethiodide in alcoholic solution, separates from absolute alcohol as a colourless, drusy mass of short, four-sided prisms, and melts without becoming brown, but with evolution of gas bubbles, at $170-171^\circ$. It is stable in the dry state, but is slowly decomposed by water, from which it may be crystallised, although a diminished yield is thus obtained and the crystals obstinately retain traces of water. In regard to its stability towards the action of water, it occupies a position intermediate between the corresponding chloride and iodide.

T. H. P.

Conversion of the additive Compounds of Cinchonine with Hydrogen Haloids into Halogen-free Bases. By ZDENKO H. SKRAUP (*Monatsh.*, 1901, 22, 253-288. Compare Abstr., 1899, i, 961).—By the action of potassium hydroxide or silver nitrate on the additive compounds of cinchonine with hydrogen chloride, bromide, or iodide, a mixture of halogen-free bases is obtained, which are isomerides of cinchonine. Of this mixture of bases, a part is soluble in ether or 50 per cent. alcohol, and a part insoluble. The soluble portion consists chiefly of α -isocinchonine, together with a small quantity of bases with one carbon atom less than cinchonine and its isomerides (compare this vol., i, 403); the insoluble portion consists mainly of *alloe*cinchonine. The quantities of the α -isocinchonine and difficultly soluble bases respectively have been determined; and the results are

summarised in the following table. The quantities are expressed as percentages of the cinchonine used.

| | Difficultly soluble. Bases. | α -isoCinchonine. |
|-------------------------------|--------------------------------|--------------------------|
| Hydrochlorocinchonine | | |
| decomposed by | | |
| (1) Potassium hydroxide | 13.3 per cent. | 42.8 per cent. |
| (2) Silver nitrate | 31.9 „ | 33.0 „ |
| Hydrobromocinchonine | | |
| decomposed by | | |
| (1) Potassium hydroxide | 23.7 „ | 40.8 „ |
| (2) Silver nitrate | 35.7 „ | 24.3 „ |
| Hydroiodocinchonine | | |
| decomposed by | | |
| (1) Potassium hydroxide | 40.8 „ | 22.3 „ |
| (2) Silver nitrate | 59.8 „ | 15.6 „ |

In discussing these results, it is pointed out that the cause of the transformation of cinchonine and of the variation in the proportion of the two classes of bases cannot be found in the original additive products of the halogen acids with cinchonine. Each of these additive compounds is a single individual. The transformation of the cinchonine must occur during the withdrawal of the hydrogen haloid. Special experiments have shown, however, that neither potassium hydroxide nor silver nitrate can bring about any change in cinchonine or its isomerides; nor does variation of the concentration of the potash, &c., alter the relative proportion of the bases produced.

The author thinks that this group of bases (cinchonine, α - and β -iso-cinchonine, and allocinchonine) are not structural but stereo-isomerides, and discusses their relationship to each other (compare this vol., i, 404).

K. J. P. O.

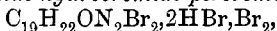
Perbromides of Cinchona Alkaloids. By A. CHRISTENSEN (*J. pr. Chem.*, 1901, [ii], 63, 313—351).—The alkaloids quinine, cinchonine, and cinchonidine yield well crystallised bromine compounds, which are acid perbromides of alkaloid dibromides, $\text{ABr}_2 \cdot 2\text{HBr} \cdot \text{Br}_2$, and thus differ from the iodine derivatives $\text{AHI} \cdot \text{I}_3$. One-sixth of the bromine is loosely combined and will set free iodine from potassium iodide, oxidise sulphurous acid, &c., and can thus be estimated.

Quinine dibromide hydrobromide perbromide, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{Br}_2 \cdot 2\text{HBr} \cdot \text{Br}_2$, prepared by adding excess of hydrobromic acid and then bromine to the solution of the alkaloid in acetic acid, crystallises in pale yellow, rhombic pyramids and prisms, which on heating decompose with the evolution of hydrogen bromide and a smell of quinoline. This substance is readily soluble in alcohol and can be crystallised from acetic acid. To aqueous sodium carbonate, 4 atoms of bromine are given up, whilst alcoholic potash withdraws the whole of the halogen. A *mercury double salt*, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{Br}_2 \cdot 2\text{HBr} \cdot \text{HgBr}_2$, obtained by rubbing the perbromide with mercury, crystallises in prismatic needles.

Quinine dibromide (Comstock and Koenigs, *Abstr.*, 1892, 1010), is obtained from the perbromide by removing bromine with sulphurous acid, and then precipitating the base with sodium hydroxide. The

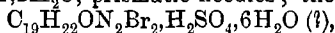
nitrate, $C_{20}H_{14}O_2N_2Br_2 \cdot 2HNO_3$, forms rhombic prisms very insoluble in water (*loc. cit.*). *Dibromoherapathite*, $4C_{20}H_{14}O_2N_2Br_2 \cdot 3H_2SO_4 \cdot 2HI \cdot I_4$, crystallises in thin plates very closely resembling herapathite.

Cinchonidine dibromide hydrobromide perbromide,



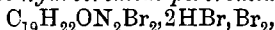
crystallises in pale yellow, quadratic plates. With mercury it yields the double salt, $C_{19}H_{22}ON_2Br_2 \cdot 2HBr \cdot HgBr_2$, crystallising in needles.

Cinchonidine dibromide, $C_{19}H_{22}ON_2Br_2$, crystallises in six-sided plates or rhombic leaflets, and begins to decompose at 180° . It does not give the quinine reaction with bromine and ammonia. The *hydrochloride*, $C_{19}H_{22}ON_2Br_2 \cdot 2HCl \cdot 2H_2O$, forms prismatic needles; the *hydrobromide*, $C_{19}H_{22}ON_2Br_2 \cdot 2HBr \cdot 2H_2O$, prismatic needles; the *sulphate*,



slender needles; the *nitrate*, $C_{19}H_{22}ON_2Br_2 \cdot 2HNO_3 \cdot H_2O$, rhombic plates.

Cinchonine dibromide hydrobromide perbromide,



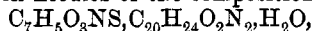
is obtained as small, yellow, prismatic needles, which give off bromine on standing in the air, leaving the hydrobromide. The *mercury* double salt, $C_{19}H_{22}ON_2Br_2 \cdot 2HBr \cdot HgBr_2$, forms long, white, prismatic needles.

Cinchonine dibromine, obtained from the perbromide, is identical with the base prepared by Comstock and Koenigs (*loc. cit.*); the *hydrobromide*, $C_{19}H_{22}ON_2Br_2 \cdot 2HBr$, crystallises in rhombic plates.

The salts of these alkaloids, when treated with a solution of potassium iodide and potassium iodate, set free a quantity of iodine equivalent to half the acid present in the salt. One mol. of the acid is therefore more loosely combined than the other. These salts are consequently acid salts, and the alkaloids are mono-acid.

K. J. P. O.

Basic Quinine "Saccharinate." By H. DÉFOURNEL (*Bull. Soc. Chim.*, 1901, [iii], 25, 606—607).—*Basic quinine "saccharinate,"* obtained by double decomposition from quinine sulphate and the sodium derivative of "saccharin" (*o*-benzoic sulphinide), crystallises from methyl alcohol in needles of the composition



which melt and decompose at 194 — 195° . It is almost insoluble in cold water, but more soluble in boiling water (1 part in 130) and in organic solvents.

N. L.

Conversion of Tropinone into *r*-Cocaine. By RICHARD WILLSTÄTTER and ADOLF BODE (*Ber.*, 1901, 34, 1457—1461).—The chief product of the action of sodium amalgam on sodium tropinonecarboxylate is *ψ-tropinonecarboxylic acid*, which probably has the betaine

structure, $\text{CH} \begin{array}{c} \nearrow \text{CH}_2 \cdot \text{CH}_2 \\ \searrow \text{NHMe} \\ \text{CH} \end{array} \text{CH} \begin{array}{c} \nearrow \text{CH} \cdot \text{CH}_2 \\ \searrow \text{CO} \cdot \text{O} \end{array}$; it is insoluble in ether, but readily

soluble in water, from which it crystallises in glistening, hexagonal, monosymmetric tablets containing $3H_2O$; when dried over sulphuric acid it melts and decomposes at 201 — 202° ; it has a neutral reaction, is stable towards potassium permanganate, and has a normal

molecular weight in aqueous solution. The *hydrochloride*, $C_9H_{15}O_3N.HCl$, crystallises from alcohol in monoclinic tablets, and melts and decomposes at 239° ; the *aurichloride* crystallises in needles, and melts and decomposes at $174-176^\circ$. The acid does not give an ester, but is converted by hydrogen chloride in alcoholic or aqueous solution into ψ -tropine.

An *inactive ecgonine*, probably racemic ecgonine, is produced as a bye-product in the reduction of tropinecarboxylic acid; it separates from alcohol in anhydrous, rhombic crystals, has a neutral reaction, is stable towards permanganate, and melts and decomposes at 251° . The *hydrochloride* forms slender, white needles containing $\frac{1}{2}H_2O$, becomes anhydrous at 120° , melts with frothing at 149° , and is more soluble in alcohol than the hydrochloride of the carbonic acid; the *aurichloride* forms glistening needles, is more soluble than the isomeride, and melts and decomposes at 213° . The *methyl ester* crystallises from ethyl acetate in needles, and melts at 125° ; the *methiodide* of the ester is readily soluble in water, crystallises in needles, melts at 182° , and is converted by warm alkalis into *cycloheptatrienecarboxylic acid*. *r-Cocaine* crystallises from light petroleum in hexagonal plates, and melts at 80° ; it forms a picrate, aurichloride, and platinichloride, and like *d-cocaine*, but unlike *l-cocaine*, gives a sparingly soluble nitrate. The *hydrochloride* crystallises from alcohol in transparent tablets and melts and decomposes at 194° . Synthetic cocaine has the same physiological action as the natural product.

T. M. L.

Stereoisomeric 2:6-Diphenylpiperidines. By MAX SCHOLTZ (*Ber.*, 1901, **34**, 1616—1623. Compare *Abstr.*, 1895, **i**, 563; Paal, *ibid.*, 1896, **i**, 389).—The base obtained by the reduction of 2:6-diphenylpyridine is a mixture of two stereoisomeric diphenylpiperidines, the one oily, and the other melting at 71° . The two are most readily separated by the fractional crystallisation of their hydrochlorides, as the salt of the oily base, which melts at 218° , is much more soluble than that of the solid, which melts at 316° . 2:6-Diphenylpiperidine melts at 71° , and distils at $206-207^\circ$ under 15 mm. pressure. The *hydrobromide* crystallises in long needles melting at 295° , the *hydriodide* melts at 248° , and is only sparingly soluble in water at 25° . The acid *sulphate*, $C_{17}H_{19}N.H_2SO_4$, crystallises in plates, and melts at 255° , the picrate melts at 212° , not 198° as previously stated, and the *benzoyl* derivative crystallises in prisms melting at 137° . When treated with *o*-xylene bromide, the base yields *xylylenediphenylpiperidonium bromide*, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} NBr \cdot C_5H_5Ph_2$, which crystallise from alcohol in glistening needles melting at 190° .

The oily base, *iso*-2:6-diphenylpiperidine, does not solidify when placed in a freezing mixture, distils at $204-205^\circ$ under 15 mm. pressure, and has a sp. gr. 1.0657 at $20^\circ/4^\circ$. The *hydrochloride* crystallises in colourless needles, and melts at 218° , the *hydrobromide* melts at 258° , the *hydriodide* at 257° , the acid *sulphate*, which is readily soluble in water, at 192° , the *benzoyl* derivative at 115° , and the *xylylenediphenylpiperidonium bromide* at 135° . The picrate is an oil. All

attempts to resolve either of the two bases into optically active constituents have so far failed. J. J. S.

Action of Benzyl Chloride and Iodide on Pyridine. By A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 249—258).—*Pyridine benzyl iodide*, C_5H_5N, CH_2PhI, H_2O , separates from 95 per cent. alcohol, by cooling or adding ether, in pale yellow crystals which melt at 97° and are soluble in water or alcohol.

By the action of excess of pyridine on benzyl chloride or iodide, a mixture of 2- and 3-benzylpyridines is obtained, the former predominating if the chloride is used, and the latter if the iodide.

2-Benzylpyridine, $C_{12}H_{11}N$, boils at 276° under 742 mm. pressure, and on cooling becomes viscid, but does not crystallise; it has a not unpleasant odour, somewhat resembling that of lemons and mixes with alcohol or ether; it has the sp. gr. 1.0536 at $20^\circ/0^\circ$ and 1.0756 at $0^\circ/0^\circ$. When oxidised with acid permanganate, it yields picolinic acid. Its salts with mineral acids are mostly readily soluble in water and difficult to crystallise; its *platinichloride* separates from water in large, orange crystals melting at 183° , and its *picrate* is deposited from alcohol in sparkling, strongly refractive, yellow crystals melting at 140° .

3-Benzylpyridine, boiling at 287° under 742 mm. pressure, resembles the 2 compound, but has a stronger and unpleasant smell; it has the sp. gr. 1.0614 at $20^\circ/0^\circ$ and 1.0756 at $0^\circ/0^\circ$. Oxidation with acid permanganate gives isonicotinic acid. It forms readily soluble salts with mineral acids; its *platinichloride* separates from water in golden-yellow leaflets melting at 207° , and the *picrate* crystallises from benzene in large, shining, plastic needles melting at about 136 — 138° .

Besides the two benzylpyridines, the action of benzyl chloride or iodide on pyridine yields a small quantity of higher boiling bases, probably dibenzylpyridines, together with neutral products which are being investigated. T. H. P.

Azoxonium Compounds. By FRIEDRICH KEHRMANN (*Ber.*, 1901, **34**, 1623—1626).—Methylcatechol [$Me : (OH)_2 = 1 : 3 : 4$] and *o*-aminom-cresol react at 250 — 260° , yielding two isomeric *dimethylphenoxazines*,

$C_6H_3Me \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} C_6H_3Me$, the one melting at 179° and the other at

204 — 205° . The reaction proceeds more readily than in the preparation of phenoxazine itself (Bernthsen, *Abstr.*, 1887, 665). When oxidised with ferric chloride or bromine, the two compounds, especially the one melting at 204 — 205° , yield salts of *dimethylphenoxazonium*.

The *picrate*, $N \begin{smallmatrix} \text{C}_6\text{H}_3\text{Me} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3\text{Me} \end{smallmatrix} \text{O} \cdot \text{O} \cdot \text{C}_6\text{H}_2\text{O}_6\text{N}_3$, forms a reddish-violet crystalline powder, the *bromide* is very similar. *Phenoxazonium picrate*,

$N \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{O} \cdot \text{O} \cdot \text{C}_6\text{H}_2\text{O}_6\text{N}_3$, is an unstable, brick-red powder; its hydrogen atoms in the para-positions to the tervalent nitrogen are readily replaceable by amino- or substituted amino-groups, yielding different coloured dyes. Phenanthroxazine (this vol., i, 280), when oxidised with bromine in nitrobenzene solution, yields *phenanthrazoxonium per-*

bromide, $C_{28}H_{16}ONBr_3$, in the form of dark blue plates with a coppery lustre. J. J. S.

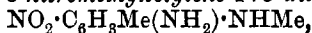
[Method of] Avoiding the Formation of Bases containing Chlorine in the Reduction of Aromatic Nitro-compounds with Tin and Hydrochloric Acid. By JOHANNES PINNOW (*J. pr. Chem.*, 1901, [ii], 63, 352—363).—When the reduction is carried out by tin and hydrochloric acid in the presence of a piece of graphite, it is found possible to operate in dilute solution and thus avoid that rise of temperature which is favorable to the production of chloro-bases. Thus 3-nitrodimethyl-*p*-toluidine under these conditions yields more dimethyltolylenediamine, and less chlorodimethyltolylenediamine, than when reduced by the ordinary method. Further, no 1:5-dimethylbenziminazole is formed at a temperature of 17° by this method, and only 3.3 per cent. at a temperature of $50-55^\circ$.

The double salt of 3-nitrodimethyl-*p*-toluidine hydrochloride and stannic chloride, $4C_9H_{12}O_2N_2 \cdot 4HCl \cdot SnCl_4 \cdot 3H_2O$, is very insoluble in water and melts and decomposes at $230-231^\circ$.

1:5-Dimethylbenziminazole tartrate, $C_8H_{10}N_2 \cdot C_4H_6O_6 \cdot 4H_2O$, forms needles melting at $187.3-188^\circ$.

When the reduction is carried out by Löb's method (*Abstr.*, 1896, i, 533), using graphite instead of platinum, chloro-bases are always formed and 30 per cent. of dimethylbenziminazole is produced.

The reduction of nitromethylaziminotoluene was also investigated. To obtain this substance, 3:5-dinitromethyl-*p*-toluidine was obtained by the action of 55 per cent. nitric acid containing nitrous acid on dimethyl-*p*-toluidine. On reduction of the dinitro-compound with ammonium sulphide, 3-nitromethyltolylene-4:5-diamine,



is produced and crystallises in bluish-red plates, or short prisms melting at $131.5-132.5^\circ$. 7-Nitro-1-methylaziminotoluene, prepared from the diamine by the action of nitrous acid, forms light brown needles melting at $174.5-175.5^\circ$. Reduction in the ordinary way with tin and hydrochloric acid produced 1-methylaziminochlorotoluidine, $C_8H_9N_4Cl$, melting at $189-190^\circ$. Reduction with zinc dust and acetic acid, followed by the addition of benzaldehyde to the reduced product, yields benzylidene-1-methylazimino-*m*-toluidine, forming yellowish-green needles melting at $151.5-152.5^\circ$. On boiling this substance with concentrated hydrochloric acid, a sparingly soluble base, melting at 278° , and amino-1-methylaziminotoluene, $NH_2 \cdot C_6H_3Me \cdot N_3Me$, are formed. The latter crystallises in white needles melting at 133.5° , and forms a hydrochloride, $C_8H_{10}N_4 \cdot HCl \cdot H_2O$.

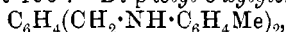
On reducing 7-nitro-1-methylaziminotoluene with tin and hydrochloric acid in the presence of graphite, at a temperature finally of 46° , a mixture of chloro-base and amino-1-methylaziminotoluene is obtained which cannot be separated. With benzenediazonium chloride, the mixture yields the hydrochloride of benzeneazoaminomethylaziminotoluene, $C_{14}H_{14}N_6$, which forms orange needles melting at 202° .

K. J. P. O.

Action of Aldehydes and of Carbonyl Chloride on Diamines. By MAX SCHOLTZ and K. JAROSS (*Der.*, 1901, 34, 1504—1513).—The

object of the following experiments was to ascertain the influence of substituents in various positions in aromatic diamines on the reaction between these and the aldehydes. Diphenyl *o*-xylylenediamine readily reacts with formaldehyde to produce *diphenyl-o-xylylene-*

methylenediamine, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{NPh} \\ \text{CH}_2 \cdot \text{NPh} \end{smallmatrix} CH_2$, which crystallises in colourless needles melting at 196° . *Di-p-tolyl-o-xylylenediamine*,



is formed together with *p*-tolylidihydroisindole, when *o*-xylylene bromide is treated with an excess of *p*-toluidine, and crystallises in colourless plates melting at 112° . With formaldehyde, it yields *di-p-tolyl-o-*

xylylenemethylenediamine, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{N}(C_6H_4Me) \\ \text{CH}_2 \cdot \text{N}(C_6H_4Me) \end{smallmatrix} CH_2$, which crystallises in plates melting at $159-160^\circ$. On the other hand, *di-o-tolyl-*

o-xylylenediamine does not form a condensation product with formaldehyde, and this is probably due to the stereochemical effect of the methyl group in the *o*-position. 1:3-*Di-p-tolyltetrahydroglyoxaline*,

$CH_2 \begin{smallmatrix} \text{N}(C_6H_4Me) \cdot CH_2 \\ \text{N}(C_6H_4Me) \cdot CH_2 \end{smallmatrix}$, is obtained from formaldehyde and *di-p-tolyl-*

ethylenediamine, and forms colourless tablets melting at 176° . 1:3-*Di-m-tolyltetrahydroglyoxaline* is prepared in a similar manner from *di-m-tolylethylenediamine*, and crystallises in colourless prisms melting at $100-101^\circ$. *Di-o-tolylethylenediamine* also appears to react with formaldehyde, but no crystalline product could be isolated from the mass produced.

Dixylylethylenediamine, $C_2H_4(NH \cdot C_6H_3Me_2)_2$, is obtained by heating *as-m*-xylylidine with ethylene bromide and sodium carbonate, and crystallises in colourless needles melting at 71° . It yields no crystalline condensation product with formaldehyde. 1:4-

Dixylylpiperazine, $C_6H_3Me_2 \cdot N \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} N \cdot C_6H_3Me_2$, is formed along with dixylylethylenediamine, and forms colourless plates melting at 150° .

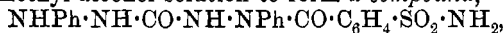
m-Tolylethylenediamine reacts with acetaldehyde in a similar manner to formaldehyde, producing 1:3-*di-m-tolyl-2-methyltetrahydroglyoxaline*, $CHMe \begin{smallmatrix} \text{N}(C_6H_4Me) \cdot CH_2 \\ \text{N}(C_6H_4Me) \cdot CH_2 \end{smallmatrix}$, which forms colourless needles melting at 83° and is very unstable.

Di-p-tolyltrimethylenediamine does not react with formaldehyde, whilst diphenyltrimethylenediamine undergoes the normal reaction. These two bases, however, do not differ in their behaviour towards other aldehydes. *Di-p-tolyltrimethylenediamine* readily reacts with propaldehyde, forming two compounds of the same percentage composition. One of these is an amorphous powder melting at 98° , whilst the second, $CH_2Et \begin{smallmatrix} \text{N}(C_6H_4Me) \cdot CH_2 \\ \text{N}(C_6H_4Me) \cdot CH_2 \end{smallmatrix} CH_2$, crystallises in short, colourless prisms, melts at 268° , and has the molecular weight corresponding with the formula given, according to which it is 1:3-*tolyl-2-ethylhexahydropyrimidine*. Diphenyltrimethylenediamine also yields two compounds with propaldehyde, one of which melts at about 90° and the other at 250° . These have not yet been more closely examined.

Di-*m*-tolylethylenediamine is converted by carbonyl chloride into *di-m*-tolylethylenecarbamide, $\text{CO} \begin{smallmatrix} \text{N}(\text{C}_6\text{H}_4\text{Me}) \cdot \text{CH}_2 \\ \text{N}(\text{C}_6\text{H}_4\text{Me}) \cdot \text{CH}_2 \end{smallmatrix}$, which forms colourless, lustrous plates melting at 146° . A small amount of a *dichloride* is also produced. Di-*o*-tolylethylenediamine, on the other hand, does not yield a cyclic carbamide derivative, but only the *dichloride* of *di-o*-tolylethylenedicarbamic acid, $\text{C}_2\text{H}_4[\text{N}(\text{COCl}) \cdot \text{C}_6\text{H}_4\text{Me}]_2$, which crystallises in colourless needles melting at 163° . Sodium ethoxide converts it into *di-o*-tolylethylenediurethane, $\text{C}_2\text{H}_4[\text{N}(\text{CO}_2\text{Et}) \cdot \text{C}_6\text{H}_4]_2$, which is a colourless, crystalline powder melting at 79° . This difference between the behaviour of the *m*-compound and the corresponding *o*-derivative is also to be referred to the stereochemical effect of the *o*-methyl group. A. H.

Electrolytic Preparation of Benzidine. By WALTHER LÖB (*Zeit. Elektrochem.*, 1901, 7, 597—603. Compare Abstr., 1900, i, 697).—Under certain conditions, azoxybenzene may be reduced to benzidine with a yield of 64 to 70 per cent. Azoxybenzene (2 grams) is suspended in 25.75 per cent. hydrochloric acid (70 c.c.) containing stannous chloride (1—1.5 grams) in solution, the liquid is placed in a porous pot standing in hydrochloric acid; the cathode is formed of pure nickel gauze, and it is also used as a stirrer in order to keep the azoxybenzene in suspension. The cathodic current density may vary from 0.008 to 0.05 ampere per sq. cm., and the temperature from 60° to 90° . Little or no benzidine was obtained when other salts were added to the solution, or other metals used as cathodes. T. E.

Action of "Saccharin" on Phenylhydrazine Ureide [Phenylcarbazide]. By H. DÉFOURNEL (*Bull. Soc. Chim.*, 1901, [iii], 25, 604—606).—Phenylcarbazide reacts with "saccharin" (*o*-benzoic sulphinide) in methyl alcohol solution to form a compound,



which crystallises in slender, white needles melting at 98° , and is decomposed by dilute sulphuric acid, or by prolonged boiling with water, with the formation of *o*-sulphaminobenzoic acid. N. L.

Thiourea-amidines. By HENRY L. WHEELER (*J. Amer. Chem. Soc.*, 1901, 23, 223—227).—Wheeler and Sanders (Abstr., 1900, i, 563) have shown that, by the action of organic bases on ureaimino-esters, amidines are produced; this is now confirmed by the preparation of phenylbenzenylureaphenylamidine from phenylcarbimide and phenylbenzenylamidine, the product being identical with that previously described.

On the other hand, the compounds obtained (*loc. cit.*) by the action of phenyl- and benzoyl-thiocarbimides on imino-esters, and supposed to be phenylbenzenylthiourea-*p*-anisylamidine, the corresponding phenyl and β -naphthyl derivatives, benzoylbenzenylthiourea-phenylamidine and the analogous *o*-tolyl derivative, are found, on further investigation, to be phenyl-*p*-anisyl-, diphenyl-, phenyl- β -naphthyl-, phenylbenzoyl-, and *o*-tolylbenzoyl-thiocarbamides respectively.

The true phenylbenzenylthiourea-phenylamidine,
 $\text{NHPh} \cdot \text{CPh} \cdot \text{N} \cdot \text{CS} \cdot \text{NHPh},$

obtained by the action of phenylthiocarbimide on phenylbenzenylamidine, crystallises from benzene in slender needles or prisms and melts at 138° ; it is quite different to the product previously described under this name. Benzoylthiocarbimide reacts with phenylbenzenylamidine to form a crystalline substance melting at 162° . E. G.

Synthesis of 1:3:4-Triazole Derivatives. By GUIDO PELLIZZARI and C. MASSA (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 363—367).—

1-Phenyl-1:3:4-triazole, $\text{NPh} \begin{smallmatrix} \text{CH:N} \\ \text{CH:N} \end{smallmatrix}$, may be obtained by the interaction of (1) formylhydrazide and formanilide, (2) diformylhydrazide and formanilide, (3) diformylhydrazide and aniline, or (4) aniline (1 mol.), hydrazine (1 mol.), and formic acid (2 mols.); it separates from benzene in long needles, or from water in hard prisms, melting at 121° , distils with partial decomposition, and dissolves readily in water or alcohol. It has no action on litmus paper, but has basic properties, and forms well-defined salts; with copper sulphate it gives a pale azure precipitate, and with mercuric chloride or silver nitrate a white precipitate. Its *platinichloride* separates in yellow needles, and on boiling in dilute aqueous solution yields the compound $(\text{C}_8\text{H}_7\text{N}_3)_2\text{PtCl}_4$ as an amorphous, yellow, insoluble powder; the *picrate* separates from alcohol in slender, yellow needles melting at 169° .

[With PAOLETTI.]—Introduced in any way into the animal (frogs and dogs) system, it acts as an excitant, producing palpitation, muscular shock, convulsions, and convulsive fits, varying in duration and intensity according to the dose administered. The minimum lethal dose is 0.06 gram per kilogram weight of animal. It thus closely resembles strychnine in its action and toxic power. T. H. P.

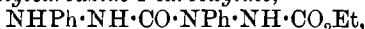
Constitution of the Urazines. By MAX BUSCH (*Chem. Centr.*, 1901, i, 933—937; from *Festschrift*, Erlangen, 1901).—Diphenylurazine was originally regarded as symmetrical diphenyldiketohexahydrotetrazine, $\text{CO} \begin{smallmatrix} \text{NPh}\cdot\text{NH} \\ \text{NH}\cdot\text{NPh} \end{smallmatrix} \text{CO}$ (Pinner, Abstr., 1888, 1084; Heller, Abstr., 1891, 1213), of which the parent substance is diphenylcarbamide (Curtius and Heidenreich, Abstr., 1895, i, 12). Later, the formula $\text{CO} \begin{smallmatrix} \text{NH}\cdot\text{NPh} \\ \text{NH}\cdot\text{NPh} \end{smallmatrix} \text{CO}$, or the tautomeric monohydroxy-modification of this, was assigned to it (Rupe, Abstr., 1896, i, 429; 1899, i, 356). From experiments described below, the author concludes that a triazole and not a tetrazine ring is present; he regards diphenyl-

urazine as phenylanilinourazole, $\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NPh}\cdot\text{CO} \end{smallmatrix} \text{N}\cdot\text{NHPh}$ or $\begin{smallmatrix} \text{N:C(OH)} \\ \text{NPh}\cdot\text{CO} \end{smallmatrix} \text{N}\cdot\text{NHPh}$.

A symmetrical constitution is excluded by the fact that isomeric products are obtained when, in one case a phenyl compound is taken and tolyl introduced, and in the other phenyl is introduced into a tolyl compound. The absence of basic properties is remarkable in diphenylurazine and its alkyloxy-derivatives; but then substances are obtained, by analogous methods, from unsymmetrical dialkylhydrazines, and

these have no basic properties either, although they must contain a five atom ring. Again, ethyl diphenylcarbazidedicarboxylate, $\text{CO}(\text{NPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2$, which could hardly form the five-membered ring, does not in fact condense to diphenylurazine. Further, the formation of a benzylidene derivative of monophenylurazine is difficult to understand if the presence of a six-membered ring is assumed; and the reaction of monoaryllurazines with nitrous acid is analogous to that of unsymmetrical disubstituted hydrazines in general.

Ethyl 2:5-diphenylcarbazine-1-carboxylate,



from ethyl chlorocarbonylphenylcarbazine, $\text{COCl}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ (Abstr., 1899, i, 957), and phenylhydrazine, melts at 186° and has no basic properties; it forms a yellowish, unstable, *mononitroso*-derivative decomposing at 121 — 122° . When heated at 200° , or digested with very dilute aqueous sodium hydroxide at 40 — 50° , it is converted quantitatively into phenylanilinourazole (diphenylurazine), which can also be prepared by warming diphenylcarbazine, $\text{CO}(\text{NH}\cdot\text{NHPH})_2$, and ethyl chloroformate with pyridine in benzene solution. This substance is a strong acid, dissolving even in aqueous alkali carbonates and ammonia; from these solutions, it is precipitated by mineral acids, but not by acetic acid. It forms *methyl* and *benzyl ethers* melting at 153° and 176 — 177° respectively; these have no acid character. It and the methyl ether form *nitroso*-derivatives which melt at 120° and 89 — 90° ; the *nitrosoamine* formed from the benzyl ether is oily.

By analogous methods, the following compounds were prepared; the numbers given are their melting points. *Ethyl 2-phenyl-5-p-tolylcarbazine-1-carboxylate*, 200° ; *phenyl-p-toluinourazole*, 238° , its *acetyl* derivative, 146 — 147° . The isomeric *5-phenyl-2-p-tolyl* compounds, 174 — 175° , $239\cdot5^\circ$, and 170° respectively. *Ethylchlorocarbonyl-p-tolylcarbazine*, 94° . *Phenylanisidinourazole*, $205\cdot5^\circ$; the isomeric *anisylanilinourazole*, 242° .

Urazoles were also obtained from ethyl chlorocarbonylphenylcarbazine by the action of methylhydrazine and of *as*-diethyl- and dibenzyl-hydrazines. Phenylmethylaminourazole has been described already as phenylurazine (Abstr., 1900, i, 314); its methyl ether forms a *benzylidene* compound melting at 139 — 140° .

Ethyl 2-phenyl-5-diethylcarbazine-1-carboxylate, 195 — 196° ; some ethoxyphenyldiazolone (Abstr., 1899, i, 957) is formed along with it. *Phenyldiethylaminourazole*, 137 — 138° ; its *ethyl ether*, 76° .

Ethyl 2-phenyl-5-dibenzylcarbazine-1-carboxylate, 135 — 136° . *Phenyl-dibenzylaminourazole*, 185 — 186° .

Methenylcarbohydrazide, $\text{CO}\langle\begin{smallmatrix}\text{NH} & \text{N} \\ \text{NH} & \text{NH}\end{smallmatrix}\rangle\text{CH}$ (Curtius and Heidenreich, Abstr., 1895, i, 12), is converted by nitrous acid into 3-hydroxy-1:2:4-triazole, $\text{OH}\cdot\text{C}\langle\begin{smallmatrix}\text{N}\cdot\text{NH} \\ \text{N} & \text{CH}\end{smallmatrix}\rangle$ (Widman and Cleve, Abstr., 1898, i, 335).

C. F. B.

Dyes for Fats. By LEONOR MICHAELIS (*Virchow Arch.*, 1901, 164, 263—270).—By a series of comparative experiments, the author has found that only azo-compounds which possess no salt-forming

group are capable of dyeing fats. Thus soudan III (azobenzene-azo- β -naphthol), benzene-azo- β -naphthol, benzene-azo-*p*-cresol, azo-*o*-tolueneazo- β -naphthol, and benzeneazophenetole, which are all insoluble in alkalis, all dye fats, whereas benzeneazo α -naphthol and benzeneazo-*o*-cresol, which are soluble in alkalis, do not act in this way. A number of these chemically indifferent dyes just mentioned are derivatives of phenols, but as they are insoluble in alkalis they probably have the tautomeric quinone structure. The benzidine dyes, such as diphenyltetrazodi- β -naphthol and diphenyltetrazodi-*p*-cresol, which are also insoluble in alkalis, also act as dyes, but are not practically convenient. The most suitable of all is azo-*o*-tolueneazo- β -naphthol, $C_6H_4Me \cdot N_2 \cdot C_6H_3Me \cdot N_2 \cdot C_{10}H_6 \cdot OH$, which is sold as scarlet R, or "Fett ponceau." A. H.

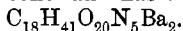
Proteids. By IVAR BANG (*Zeit. physiol. Chem.*, 1901, **32**, 79—80). By ALBRECHT KOSSEL (*ibid.*, 81).—Polemical. J. J. S.

Proteids. By ADOLF JOLLES (*Ber.*, 1901, **34**, 1447—1448; *Zeit. physiol. Chem.*, 1901, **32**, 361—392).—Four types of nitrogen compounds are produced by the oxidation of proteids (this vol., i, 262), namely, (1) ammonia (traces only), (2) carbamide, (3) substances such as methylamine and aminoacetic acid which are precipitated by phosphotungstic acid, (4) substances not precipitated by phosphotungstic acid. The proportions of nitrogen in each form found were as follows:

| | (2) | (3) | (4) | Total. |
|-------------------------------|-------|------|------|--------|
| Crystallised egg-albumin ... | 11.80 | 3.12 | — | 14.98 |
| Crystallised serum-globulin. | 12.00 | 3.93 | — | 15.94 |
| Crystallised serum-albumin. | 12.97 | 3.18 | — | 16.04 |
| Oxyhæmoglobin | 15.43 | 1.50 | — | 16.91 |
| Casein | 11.12 | 3.90 | — | 15.30 |
| Fibrin | 7.56 | 4.09 | 4.87 | 16.64 |
| Vitellin from yolk of egg ... | 11.96 | 3.21 | — | 15.30 |
| Vitellin from plants | 8.22 | 3.23 | 6.19 | 17.98 |

The production of carbamide in quantities varying from 45 to 90 per cent. of the total nitrogen is of importance as indicating the presence of $-CO \cdot NH-$ groups. T. M. L.

Breaking down of Albuminoids or Protoplasmides. By ALEXANDRE ÉTARD (*Compt. rend.*, 1901, **132**, 1184—1187).—When decalcified beef bone is boiled with dilute sulphuric acid (20:100) for several hours and the product is treated with excess of barium hydroxide, it yields glycine, leucine, a little tyrosine, a syrupy substance very soluble in methyl alcohol, and a deliquescent substance, which is quite insoluble in methyl alcohol and has the composition



When the barium is removed from the latter by treatment with sulphuric acid and methyl alcohol, a white, deliquescent, granular, crystalline substance of the composition $C_{18}H_{35}O_{15}N_5$ is obtained, which the author calls *bos-osteoplasמיד*. One mol. combines with one mol. of barium oxide, yielding $C_{18}H_{35}O_{15}N_5 \cdot BaO$. The author regards these substances, derived from albuminoids or protoplasmides,

as nitrogenous saccharides, the hydrolysis of the albuminoids being analogous to that of the condensed saccharides. C. H. B.

Detection of Cystin and of Cystein in the decomposition Products of Proteids. By GUSTAV EMBDEN (*Zeit. physiol. Chem.*, 1901, 32, 94—103. Compare Mörner, *ibid.*, 28, 595).—The author adopts a somewhat modified form of Mörner's latest method for the isolation of cystin. Horn shavings are boiled for several hours with concentrated hydrochloric acid, neutralised with sodium hydroxide, kept for 24 hours, filtered, the filtrate slightly acidified with hydrochloric acid, and evaporated to crystallisation. The crystals are first treated with water, and then with very dilute nitric acid in order to remove admixed tyrosine. Cystin may also be isolated in the form of its insoluble *copper* salt, which crystallises in at least two distinct forms. Cystein is also present in the products formed when serum-albumin, egg-albumin, or edestin is boiled with hydrochloric acid. J. J. S.

Combination of Fat and Proteid. By JOSEPH NERKING (*Pflüger's Archiv*, 1901, 85, 330—344).—After removal of the fat from proteid by a Soxhlet's apparatus, and subsequent peptic digestion, the residue yielded no ethereal extract in the majority of proteid materials investigated, namely, serum-albumin, proteids of muscle, casein, lactalbumin, oxyhæmoglobin, egg-albumin, ovomucoid, and various vegetable proteids. A few proteid substances like mucin and serum-globulin gave a small yield of ethereal extract (fat) in the same circumstances. Whether this fat is in chemical union with the proteid is not proved. W. D. H.

Formation of Urea by the Oxidation of Albumin by means of Ammonium Persulphate. By LOUIS HUGOUNENQ (*Compt. rend.*, 1901, 132, 1240—1241).—To ammoniacal aqueous solutions of egg-albumin maintained at a temperature of 90°, sufficient ammonium persulphate is added to completely oxidise the albumin. From the product of the reaction, urea was isolated, by evaporating, and extracting with alcohol-ether; it represents 5 per cent of the albumin oxidised.

K. J. P. O.

Optical Activity of Lecithin. By C. ULPANI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 368—375).—For the preparation of lecithin from yolk of egg, the author makes use of Strecker's method of extraction with a mixture of alcohol and ether. The distillation of the latter is, however, done away with, as in the event of the lecithin being optically active the heating would be liable to cause racemisation. The lecithin is separated in the form of its cadmiochloride, which, after purification, is suspended in alcohol and treated with either lead hydroxide or moist silver oxide; in the latter case, a solution perfectly free from cadmium or chlorine is obtained. This solution of lecithin is dextrorotatory, but it was not found possible to separate from it an appreciable quantity of lecithin, although voluminous white flocks are precipitated when the liquid is cooled by means of solid carbon dioxide and liquid air. For the rotation of the cadmiochloride, determined in alcoholic carbon disulphide, the following numbers were obtained: $[\alpha]_D^{28} (c\ 0.9968) + 11.41^\circ$; $[\alpha]_D^{26} (c\ 1.9936) + 11.41^\circ$; $[\alpha]_D^{24} (c\ 3.0224) + 11.29^\circ$.

These results show that lecithin is really optically active, the inactive products previously obtained being due to racemisation brought about by heating during the preparation. The asymmetric formula must hence be assigned to lecithin, which is the first mixed compound ether known to exhibit optical activity.

T. H. P.

Spectral Reactions of Blood in presence of Formaldehyde. By BERNHARD TOLLENS (*Ber.*, 1901, **34**, 1426—1427).—The difficulty of observing the absorption band of the reduced hæmoglobin of blood, which is broader but weaker than those of oxyhæmoglobin, is removed if formaldehyde is added to the liquid. The presence of this compound does not interfere in the slightest degree with the two oxyhæmoglobin absorption bands, but when the solution is gently heated with ammonium sulphide, these two bands gradually disappear and almost exactly midway between them a third black band of nearly the same intensity comes into view. If now the cooled liquid is shaken in the air, this new band vanishes and the two oxyhæmoglobin bands reappear; the latter give way to the middle band when the liquid is warmed, and so on. In presence of carbon monoxide, this action of formaldehyde does not take place, for the two carbon monoxide-hæmoglobin bands then persist even after warming with ammonium sulphide.

T. H. P.

Hexon Bases in Heteroalbumose and in Peptone (Deuteroalbumose). By H. C. HASLAM (*Zeit. physiol. Chem.*, 1901, **32**, 54—58).—Kossel and Kutscher's method for estimating hexon bases has been employed in the case of heteroalbumose and also of deuteroalbumose, both of which were obtained from Witte's peptone.

The percentages found were :

| | Histidine. | Arginine. | Lysine. | Ammonia. | Humin nitrogen. |
|----------------------|------------|-----------|---------|----------|--------------------|
| Deuteroalbumose ... | 1.5 | 7.1 | 6.9 | 0.98 | 6.5 |
| Heteroalbumose | 2.2 | 4.9 | 3.5 | 0.79 | 14.8 |

J. J. S.

Preparation of pure Amphopeptone. By PAUL MÜHLE (*Chem. Centr.*, 1901, i, 1205; from *Diss. Leipzig*).—By employing Siegfried's method of precipitating the iron salts (this vol., i, 57) two peptones, $C_{21}H_{34}O_9N_6$ and $C_{21}H_{35}O_{10}N_6$, have been isolated from the product of the peptic digestion of fibrin. The pure amphopeptones form white powders, are not deliquescent, and have distinctly acid characters. They do not form silver salts of constant composition, but the barium salts, $(C_{21}H_{33}O_9N_6)_2Ba$ and $(C_{21}H_{35}O_{10}N_6)_2Ba$, and the zinc salts, $(C_{21}H_{33}O_9N_6)_2Zn$ and $(C_{21}H_{35}O_{10}N_6)_2Zn$, have been prepared. Amphopeptone has $[\alpha]_D - 27.24$. Molecular weight determinations by Beckmann's method confirmed the formulæ quoted. By the action of fuming hydrochloric acid on amphopeptone, lysine and arginine (?) were obtained together with tyrosine.

E. W. W.

Organic Chemistry.

Action of Nitrous Acid on Propylene; Propylene Nitrosite. By NICOLAUS I. DEMJANOFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 275—279).—By passing nitrogen trioxide, prepared from nitric acid and arsenic trioxide, through an ethereal solution of propylene, *propylene nitrosite*, $C_3H_6O_3N_2$, is obtained; it crystallises from ethyl acetate in shining, white prisms which melt and evolve gas at 119—120°. On reduction with tin and hydrochloric acid, it is converted into propylenediamine.

From this and earlier results, the author concludes that when acted on by nitrous acid, hydrocarbons of the types $R \cdot CH : CH_2$ and $R \cdot CH : CH \cdot R$ yield nitrosites of the formula $C_nH_{2n}N_2O_3$, whilst hydrocarbons having the constitution $R_2 : C : CH \cdot R$ or $R_2 : C : C : R_2$ give nitrosates of the composition $C_nH_{2n}N_2O_4$.
T. H. P.

Propylhexamethylene. By NICOLAI KURSANOFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 410—412; *Ber.*, 1901, **34**, 2035—2036).—Propylhexamethylene, obtained together with hexanaphthylene and an unsaturated hydrocarbon of higher boiling point when zinc propiodide acts on chlorohexamethylene, boils at 155—156° under 730 mm. pressure; Sabatier and Senderens (this vol., i, 263) gave 153—154°. It has a sp. gr. 0.7996 at 0°/0° and 0.7865 at 20°/0°. It exhibits all the properties of the naphthenes and is slowly dissolved in nitric acid of sp. gr. 1.53, whilst with bromine in presence of aluminium bromide it yields an oily bromide.
T. H. P.

Action of Cuprous Salts on Hydrocarbons and Carbon Monoxide. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1901, [vii], **23**, 32—39).—A hydrochloric acid solution of cuprous chloride containing its constituents in the proportions corresponding with the formula $CuCl, 3.42HCl, 17.5H_2O$, when maintained for 8 days in contact with carbon monoxide under the ordinary pressure and at a temperature of 8°, absorbs about 50 times its volume of the gas, the relation between the two reagents being expressed molecularly in the following manner, $CuCl, 0.87CO$. On examining the product, it is found that the gas exists partly in solution and partly in the crystallised compound, $2CuCl, CO, H_2O$.

The maximum absorption of acetylene effected under similar conditions by a cuprous chloride solution of the concentration indicated, agrees with the relationship $3CuCl, C_2H_2$; in the case of ethylene, the ratio is $CuCl, 0.17C_2H_4$. The absorption of propylene by the cuprous solution is very slow at the commencement, but goes on increasing until after 63 days the ratio is $CuCl, 0.25C_3H_6$. A similar reaction is observed in the case of trimethylene, the ratio after 63 days being $CuCl, 0.33C_3H_6$. An excess of trimethylene, when maintained in contact with the cuprous chloride, is partly dissolved and partly converted into propylene. The action of cuprous chloride on propylene and trimethylene does not end with the formation of substances corresponding with the compound $2CuCl, CO$, and dissociating

when subjected to changes of pressure or temperature. The cuprous liquid containing either of the two hydrocarbons does not evolve any gas when diluted or boiled; it seems to contain some ethereal product united with the copper salt. G. T. M.

Action of Acetylene on Cuprous Chloride dissolved in a neutral solution of Potassium Chloride. By R. CHAVASTELON (*Compt. rend.*, 1901, 132, 1489—1492. Compare Abstr., 1900, i, 470).—When a current of acetylene plays over the surface of a saturated solution of cuprous and potassium chlorides, a purple precipitate is produced consisting of the compound $C_2H_2 \cdot Cu_2Cl_2 \cdot Cu_2O$, and the solution becomes acid. On passing the gas into the liquid and thoroughly agitating the mixture, the purple precipitate becomes rapidly converted into the yellow crystals, $C_2H_2[(Cu_2Cl_2)_2 \cdot KCl]_2$. When the solutions are diluted, the purple precipitate is produced whether the mixture is agitated or not. G. T. M.

Acetylenoid Metallic Radicles. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 1525—1527).—Recent experiments confirm the view that the acetylides C_2M_2 and C_2MH correspond with the sulphides SM_2 and SMH , and the metallic ammonia derivatives NM_3 , NM_2H , and NMH_2 . Many of the compounds of the acetylides may be regarded as containing a radicle of the type C_2R_3 , this group being analogous to the substituted ammonium radicle NR_4 . The simple and double nitrates, sulphates, chlorides, and iodides of silver acetylide may be considered to contain the radicle C_2Ag_3 , whilst the cuprous salts have the groups C_2Cu_3 , C_2HCu_2 , and C_2H_2Cu . The double iodide may be written $C_2Cu_3I \cdot CuI$, and Chavastelon's compounds (compare Abstr., 1900, ii, 470, and preceding abstract) may be formulated in the following manner, $(C_2H_2Cu)Cl \cdot CuCl$, or $C_2HCu_2Cl \cdot HCl$, and $(C_2Cu_3)Cl \cdot CuCl \cdot H_2O$, or $(C_2Cu_3)CuCl_2 \cdot H_2O$, this compound corresponding with the author's salts $(C_2Ag_3)Cl \cdot AgCl$ and $(C_2Cu_3)I \cdot CuI$ (Abstr., 1900, i, 324). The more complex derivatives studied by Chavastelon may be similarly represented. G. T. M.

Action of Nitric Acid on Acetylene. By GIUSEPPE TESTONI and L. MASCARELLI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 442—444. Compare Baschieri, Abstr., 1900, i, 534).—By passing acetylene into nitric acid of sp. gr. 1.52 in a flask immersed in water until the acid assumes a dark green colour, and then gradually pouring it into a large volume of cold water, besides nitroform and the neutral substance, $C_6H_4O_3N_4$, obtained by Baschieri (*loc. cit.*), the following compounds are formed:

(1) A straw-yellow, explosive substance melting at 78° without decomposition; when crystallised from benzene or light petroleum, copious evolution of nitrous fumes occurs, and transparent, colourless crystals of a neutral compound, $C_4H_2O_3N_4$, melting at 108° , separate; this compound, which has the normal molecular weight in acetic acid or benzene, can be crystallised unchanged from boiling water and is readily soluble in the organic solvents.

(2) A monobasic acid, $C_4H_3O_3N$, separating from toluene in large, faintly yellowish crystals melting at 149° ; it dissolves readily in

alkalis and in the ordinary solvents, and has the normal molecular weight in freezing acetic acid, whilst its aqueous solution has a strong acid reaction and can be titrated with potassium hydroxide. It forms a stable *silver* salt which forms a yellowish, curdy precipitate melting and decomposing with a slight explosion at about 165°. T. H. P.

Propyl- ψ -nitrole and *s*-Tetramethyldinitroazoxymethane. By A. SCHÖFER (*Ber.*, 1901, **34**, 1910—1914).—Propyl- ψ -nitrole, which is best prepared by the action of an aqueous solution of nitrous acid on acetoxime, yields acetoxime when treated with alcoholic sodium hydroxide or when reduced by means of aluminium amalgam. The nitrole, when treated with aniline or benzylamine, yields diazoaminobenzene or benzaldehyde respectively. *s*-Tetramethyldinitroazoxymethane boils at about 100° under 25 mm. pressure with slight decomposition, is only reduced by zinc dust and acetic acid, is not changed by potassium hydroxide or fuming nitric acid, but is decomposed by bromine and by concentrated sulphuric and hydrochloric acids. R. H. P.

Etherification by Means of Inorganic Salts. By GIUSEPPE ODDO (*Gazzetta*, 1901, **31**, i, 285—374).—The author gives first a historical account of the etherification of alcohol, and then the conclusions drawn from a large number of experiments on etherification by inorganic salts. He finds that the degree of readiness with which alcohols are etherified increases with their molecular weight, and is also influenced by the presence in the molecule of a side chain in a neighbouring position to the hydroxyl group; the collateral chains render the hydroxyl less readily mobile, and when this group is removed by a more or less energetic reagent, there is a tendency for the tension holding together the atoms in the molecule to be released and further breaking down to occur. Thus *isobutyl* alcohol, when treated at 200° with anhydrous copper sulphate, yields *isobutyl* ether together with a little *isobutane*, whilst with ferric chloride or stannous sulphate it gives only *diisobutene*. A similar influence is exerted on the hydrogen atom of the CH group in *isoamyl* alcohol, which, with the last-named salt, yields *dimethylallene*.

The fatty alcohols used by the author were methyl, ethyl, propyl, *n*-butyl, *isobutyl*, *isoamyl*, *n*-heptyl, *n*-octyl, and cetyl; it is found that all the saturated, primary, aliphatic alcohols are etherified at 200° by some of the salts of the heavy metals, and often by very small proportions of these salts.

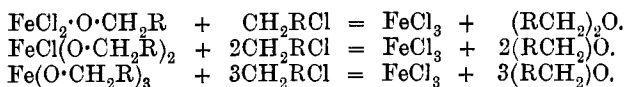
The etherifying action of a large number of compounds on benzyl and cumyl alcohols was investigated, the main bulk of the author's experiments being made with these two alcohols. None of the inorganic oxides and hydroxides having a basic character (sodium, calcium, and zinc oxides, potassium, ferric, and stannous hydroxides) have any etherifying action on these alcohols even on long boiling; antimony and arsenic trioxides act slowly and to some extent as reducers, whilst phosphoric oxide etherifies them very rapidly even when traces of it only are present; the chlorides of the alkali and alkaline earth metals are quite inactive, whilst nickel chloride and zinc iodide tend to bring about more complex condensations, and silver chloride etherifies cumyl alcohol readily, but is without action on benzyl alcohol; of the other

chlorides, that of magnesium has but a slight action, those of cobalt, cadmium and iodine, and mercuric and mercurous chlorides act slowly, but give good yields of ether, whilst the chlorides of copper, aluminium, and antimony and sulphur monochloride act still better, and stannous, stannic, ferric, and zinc chlorides give the best results. Hydrochloric acid and alkyl chlorides etherify but slowly, whilst sulphuric acid, even traces of it, acts very rapidly. The sulphates show actions similar to those of the corresponding chlorides. In the aromatic, as in the aliphatic series, the degree of readiness with which the alcohols undergo etherification increases with the molecular weight, and for alcohols containing an equal number of carbon atoms in the molecule, one belonging to the aromatic series is more readily etherified than one of the aliphatic series.

The results of the author's measurements lead to the conclusion that the power to cause etherification of the primary saturated alcohols is possessed by salts of the heavy metals and of magnesium formed with energetic acids, and this is more especially the case with those tending to form basic salts. At the temperature of 200°, all the normal salts of the alkali and alkaline-earth metals are inactive, as are also their oxides, basic hydroxides, and carbonates.

The author finds further that along with the increasing readiness of the alcohols to etherify as the molecular weight and the complexity of the space formula of the alcohol increase, there is a corresponding diminution in the stability of the ether formed.

After discussing the various hypotheses which have from time to time been put forward to explain the mechanism of etherification, the author gives his own views on the subject. In the case of ferric chloride, for example, he considers the action on alcohol to consist of the replacement of the chlorine atoms by radicles, $\cdot\text{O}\cdot\text{CH}_2\text{R}$, hydrogen chloride being evolved, and the compounds $\text{FeCl}_2\cdot\text{O}\cdot\text{CH}_2\text{R}$, $\text{FeCl}(\text{O}\cdot\text{CH}_2\text{R})_2$, and $\text{Fe}(\text{O}\cdot\text{CH}_2\text{R})_3$, being formed; the hydrogen chloride may, under favourable conditions, react with the alcohol, yielding an alkyl chloride, which with the above compounds gives ferric chloride and the ether corresponding with the alcohol, thus:



These views are supported by the fact that in all the cases examined the formation of hydrogen chloride and alkyl chloride was observed; the metallic alkoxides are unstable and difficult to isolate, but their existence is indicated by the formation of benzyl ethyl ether when benzyl alcohol is treated with ferric chloride and ethyl iodide. Similar explanations hold for the etherification produced by other salts.

The experimental results are given in detail.

T. H. P.

Contact Action and the Secondary and Tertiary Alcohols. By AUGUSTE TRILLAT (*Compt. rend.*, 1901, 132, 1495—1497. Compare this vol., i, 441).—The vapour of *isopropyl* alcohol, when mixed with air and passed over a heated platinum spiral, undergoes oxidation, the yield of acetone being 16 per cent. *sec.* Butyl alcohol, when

similarly treated, yielded a small quantity of methyl ethyl ketone, whilst *sec*.octyl alcohol (methylhexylcarbinol) gave rise to methyl hexyl ketone; *sec*.amyl alcohol furnished traces of a ketonic compound which was not identified.

tert.Butyl alcohol under these conditions is oxidised, yielding acetone and formaldehyde. Since acetone itself, when oxidised by oxygen in contact with the heated spiral, yields formaldehyde, this product, in the preceding example, may be derived either directly from the alcohol, $\text{CMe}_3\cdot\text{OH} + 2\text{O} = \text{CMe}_2 + \text{CH}_2\text{O} + \text{H}_2\text{O}$, or by a secondary oxidation of the ketone. The amount of acid produced is negligible.

tert.Amyl alcohol, $\text{CMe}_2\text{Et}\cdot\text{OH}$, behaves similarly, also giving rise to acetone and formaldehyde. G. T. M.

Active Erythritols. By LÉON MAQUENNE and GABRIEL BERTRAND (*Compt. rend.*, 1901, 132, 1419—1421).—The active erythritols (Abstr., 1900, ii, 423, 424, 472) are identical in crystalline form, and show faces of the hexagonal prism e^2 , and of the rhombohedron p without any trace of hemihedrism. Both are negatively uniaxial. *d*-Erythritol [$1:0\cdot48005$; $pp = 130^\circ 20'$, $pe^2 = 119^\circ 4'$], *l*-erythritol [$1:0\cdot47820$; $pp = 130^\circ 30'$, $pe^2 = 119^\circ$].

In both cases, the rotatory power in alcoholic solution is opposite in sign to the rotatory power in aqueous solution. *l*-Erythritol in water has $[\alpha]_D +4^\circ 33$, in alcohol of 90° $[\alpha]_D -10^\circ 5$ and in alcohol of 95° , $-11^\circ 50$, whilst for *d*-erythritol the corresponding values are $-4^\circ 40$, $+10^\circ 10$, and $+11^\circ 10$.

The tetracetins of the active erythritols are syrupy and non-crystallisable; when dissolved in chloroform, the values of $[\alpha]_D$ are $+21^\circ 6$ and $-19^\circ 28$ respectively. The dibenzoic acetals crystallise in slender, white needles melting at 231° and subliming slowly even at 200° . The divaleric acetals crystallise in nacreous plates melting at 105 — 106° .

When oxidised with nitric acid, *d*-erythritol yields ordinary tartaric acid, whilst *l*-erythritol yields a tartaric acid with equal optical activity of opposite sign. All the active compounds described above yield racemic modifications. C. H. B.

Racemic Erythritol. By LÉON MAQUENNE and GABRIEL BERTRAND (*Compt. rend.*, 1901, 132, 1565—1567).—The authors, being in possession of a stereoisomeric pair of erythritols, have synthesised the racemic compound formerly obtained by Griner from the stereoisomeric crotonylene dibromides (Abstr., 1893, i, 450; 1894, i, 62). The inactive substance is more soluble than its components; it is probably a pseudoracemic compound, and may be caused to separate from its saturated solutions by the addition of traces of either of the active forms.

The properties of the tetracetyl, dibenzylidene and diheptylidene derivatives of the authors' racemic compound agree entirely with those of the corresponding compounds prepared by Griner. G. T. M.

Constitution of mixed Carbonic Esters of Alcohols and Phenols. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1901, [iii], 25, 632—636).—An attempt to show that the two hydroxyl groups of

carbonic acid are not identical in function, one being acidic and the other alcoholic.

T. M. L.

Optical Activity of Lecithin. II. By C. ULPANI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 421—425. Compare this vol., i, 491).—Lecithin cadmiochloride, prepared as previously described (*loc. cit.*), gives on analysis results agreeing well with numbers for a lecithin containing either two stearic acid residues or two oleic acid residues. On decomposing the compound with barium hydroxide and treating the soap formed with hydrochloric acid, a mixture of stearic and oleic acids is obtained. Whether both the acids occur in the same lecithin molecule or whether several lecithins exist containing different fatty acids is as yet uncertain.

T. H. P.

Calcium Glyceroarsenate. By CAMILLE PAGEL (*J. Pharm.*, [vi], 13, 449—452).—With the view of administering arsenic in a form analogous to glycerophosphoric acid, the author has prepared calcium glyceroarsenate, $C_3H_5(OH)_2 \cdot O \cdot AsO_3Ca, 2H_2O$, by heating a mixture of glycerol and arsenic acid for several days, then neutralising with milk of lime, filtering, evaporating, and precipitating with 95 per cent. alcohol. The dried product is a powder, insoluble in water and in alcohol, but readily soluble in mineral and organic acids, and especially in a weak solution of citric acid. The arsenic which it contains cannot be detected by ammonium molybdate or by hydrogen sulphide.

M. J. S.

Manganic Acetate. By ODIN T. CHRISTENSEN (*Zeit. anorg. Chem.*, 1901, 27, 321—340).—See this vol., ii, 512.

Dry Distillation of the Salts of Fatty Acids. By WALTHER DILTHEY (*Ber.*, 1901, 34, 2115—2125).—Calcium valerate (900 grams) yields on dry distillation an oily distillate (287 grams) consisting of a mixture of ketones and aldehydes, accompanied by a gaseous product which, when passed through bromine, gives rise to 323 grams of olefine dibromides, the residual gas consisting of carbon monoxide, methane, ethane, and hydrogen. The olefines consist chiefly of the butylenes, accompanied by smaller quantities of ethylene, propylene, and traces of the higher homologues; these hydrocarbons were identified by an examination of their bromine and iodine derivatives. The mixture of aldehydes and ketones contains the following compounds: Valeraldehyde, valerone, methyl isobutyl ketone, the ketone $C_7H_{14}O$, probably a methyl amyl ketone, an isomeride of valerone, and notable quantities of the higher ketones. The unsaturated aldehyde, α -isopropyl- β -isobutylacetaldehyde, could not be detected amongst the products of distillation; this substance, when present in a mixture, is readily identified by means of its condensation product, $C_{17}H_{25}O_7N_7$, with aminoguanidine, this derivative crystallising from alcohol in yellow needles.

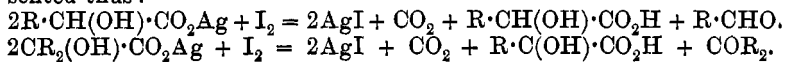
On dry distillation, a mixture of potassium isovalerate and sodium acetate yields carbon monoxide, hydrogen, methane, butylene, isopropyl alcohol, and a mixture of ketones consisting chiefly of methyl isobutyl ketone.

G. T. M.

Preparation of Acid Anhydrides by the aid of Tertiary Amines. By EDGAR WEDEKIND (*Ber.*, 1901, 34, 2070—2077).—The acid chlorides react with tertiary amines, forming the hydrochloride of the amine and the acid anhydride, if sufficient water be present in the mixture. In some cases, the anhydride can be obtained by mixing the acid chloride and amine, filtering from the hydrochloride which separates out, and then adding the requisite amount of water to the filtrate, which probably contains an unstable intermediate product of the type $CR_2\cdot CO$. *iso*Butyric anhydride is readily formed when the corresponding chloride is mixed with pyridine in ethereal solution, the pyridine hydrochloride filtered off, and cold water added, and *iso*-valeric anhydride can be prepared in a similar manner. α -Bromopropionic anhydride and α -bromoisobutyric anhydride can also be prepared by treating the chlorides with pyridine in ethereal solution and pouring the mixture on to ice. Cinnamic anhydride is best prepared by mixing the chloride with pyridine and treating the compact mass with warm water. Phenylacetic chloride also reacts in a similar manner, but the anhydride is not always produced, the reaction being evidently a complicated one; diphenylacetone is always obtained in the reaction, and is probably formed by the decomposition of pyridine phenylacetate on distillation.

Diphenylacetonesemicarbazone crystallises in pointed needles or silvery plates melting at 145—146°. A. H.

Action of Iodine on the Silver Salts of Hydroxy-acids. By R. O. HERZOG and R. LEISER (*Monatsh.*, 1901, 22, 357—360).—The reaction of the silver salts of α -hydroxy-acids with iodine are represented thus:



Lactic acid yields aldehyde; glycollic acid, formaldehyde; mandelic acid, benzaldehyde, and α -hydroxyisobutyric acid, acetone. In all cases, the reaction takes place with ease, and the aldehyde or ketone is readily isolated. From glyceric acid ($\alpha\beta$ -dihydroxypropionic acid) glycolaldehyde is not obtained, but formaldehyde. K. J. P. O.

Production of Methylsuccinic Acid from Pyruvic Acid. By LUDWIG WOLFF (*Annalen*, 1901, 317, 22—26. Compare this vol., i, 502).—Pyruvic acid, after purification by repeated distillation under 15 mm. pressure, yields only traces of methylsuccinic acid when heated to its boiling point under atmospheric pressure, but when treated with hot concentrated hydrochloric acid, a notable quantity of the dibasic acid is produced; a yield of 60 per cent. is obtained when the ketonic acid is first converted into α -ketovalerolactone- γ -carboxylic acid, the intermediate compound being heated with the mineral acid for 1 hour at 120°. A smaller yield is obtained on heating the intermediate product with water at 120°; pyruvic acid itself, under these conditions, does not give rise to any methylsuccinic acid. G. T. M.

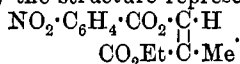
α -Hydroxy- β -butenoic Acid (Vinylglycollic Acid) and its Decompositions. By G. VAN DER SLEEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 79—83).—The nitrile of α -hydroxy- β -butenoic

acid boils at 93—94° under 16—17 mm. pressure, and forms an *acetate* when treated with acetic anhydride. Both the nitrile and its acetate are converted into the *amide* of α -hydroxy- β -butenoic acid by the action of concentrated hydrochloric acid; this melts at 80·8° and when hydrolysed yields the *acid*, which crystallises in needles, boils at 125—130° under 12—13 mm. pressure, has a dissociation constant 0·046, and forms an *ethyl ester* boiling at 173° under 756·5 mm. pressure. The *dibromo-amide* does not melt, but chars when heated; the *dibromo-acid* melts at 121—121·5° and yields α -hydroxybutyric acid when reduced with sodium amalgam. α -Hydroxybutenoic acid when treated with strong acids, yields propionylformic acid, which melts at 31·5—32°, boils at 73—75° under 15 mm. pressure, and forms a *phenylhydrazone* melting at 143—144°, and an *oxime* melting and decomposing at 154°; *ethyl propionylformate* boils at 66—67° under 16 mm. pressure, and forms a *phenylhydrazone* melting at 191°. When α -hydroxybutenoic acid is treated with alkalis, a crystalline *acid* (probably 2-hydroxy- Δ^3 -tetrahydrophthalic acid) is formed; it melts at 142—142·5°, and loses a mol. of carbon dioxide forming a syrupy *acid* (probably *o*-ketohexahydrobenzoic acid), which forms a *phenylhydrazone* melting at 159°, an *oxime* decomposing at about 177°, and by further elimination of carbon dioxide yields an oil (probably cyclohexanone). R. H. P.

Geometrically Isomeric Derivatives of Ethereal Formylpropionates. By WILHELM WISLICENUS and CHARLES L. WOLFF (*Annalen*, 1901, 316, 333—336. Compare Abstr., 1900, i, 597, and this vol., i, 361).—Ethyl formylpropionate resembles ethyl formylacetate in yielding two isomeric *p*-nitrobenzoates when its sodium derivative is treated with *p*-nitrobenzoic chloride.

The α -compound is obtained when the condensation is effected in cold dry ether free from alcohol; it crystallises from alcohol and melts at 120—121°. The β -compound is produced either by heating its isomeride at 240—250° in sealed tubes, or by the direct action of *p*-nitrobenzoic chloride on the sodium derivative of ethyl formylpropionate dissolved in a dilute aqueous sodium hydroxide solution; it crystallises from alcohol, melts at 140—142°, and can be heated to 250° without undergoing any change.

The configuration $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \underset{\text{Me} \cdot \text{C} \cdot \text{CO}_2 \text{Et}}{\overset{\text{C} \cdot \text{H}}{\text{C}}}$, in which the acidic groups are arranged on opposite sides of the ethylenoid carbon atoms, is ascribed to the more stable β -derivative, the labile α -isomeride having in all probability the structure represented by



G. T. M.

Nitration of Ethereal Acetoacetates and their Acyl Derivatives. By LOUIS BOUVEAULT and A. BONGERT (*Compt. rend.*, 1901, 132, 1569—1572. Compare this vol., i, 311).—The two isomeric methyl butyrylacetoacetates yield on nitration the compound $(\text{C}_3\text{H}_2\text{O}_3\text{N})_2$; this substance is an oil boiling at 151° under 10 mm. pressure and having a sp. gr. 1·429 at 0°/4°; its molecular weight

was determined by the cryoscopic method in benzene. On treatment with aqueous ammonia solution, the preceding ester is transformed into an *amide*, $C_4H_4O_4N_2$, melting at 253° .

Ethyl diacetylacetate when nitrated yields an *ethyl ester* boiling at 161° under 10 mm. pressure, and having a sp. gr. 1.296 at $4^\circ/0^\circ$; this compound on treatment with ammonia yields the amide melting at 253° . The new ethyl ester is also produced by nitrating ethyl acetoacetate; it is also a by-product in the preparation of ethyl nitroacetate (Abstr., 1900, i, 5). These results are most readily explained by assuming the formation of the nitro-ester, $NO_2 \cdot CHAc \cdot CO_2Me$, during the nitration of methyl acetoacetate; by hydrolysis, this product would give rise to methyl nitroacetate, $NO_2 \cdot CH_2 \cdot CO_2Me$, which, under the influence of mineral acids, undergoes condensation with the elimination of water, $2NO_2 \cdot CH_2 \cdot CO_2Me = 2H_2O + C_8H_6O_6N_2$.

G. T. M.

Synthesis of $\alpha\beta\gamma$ -Trihydroxybutyric Acid [Erythric Acid].

By C. PREY (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 77—78).— $\alpha\beta\gamma$ -Trihydroxybutyric acid has been synthesised by treating the amide of α -hydroxybutenoic acid (compare this vol., i, 499) with an alkaline solution of potassium permanganate. Various halogen compounds of the type $CH_2X \cdot CHX \cdot CH(OH) \cdot CONH_2$ were prepared, but none gave erythric acid when hydrolysed.

R. H. P.

Behaviour of Alkylene Oxides towards Ethyl Malonate and Ethyl Acetoacetate. By WILHELM TRAUBE and ERICH LEHMANN (*Ber.*, 1901, 34, 1971—1983. Compare Abstr., 1899, i, 417).—*Ethyl butyrolactonecarboxylate* [lactone of ethyl γ -hydroxyethylmalonate],

$CH_2 \cdot CH_2 \cdot \begin{array}{c} O \\ \diagup \quad \diagdown \\ CO \end{array} > CH \cdot CO_2Et$, prepared by the action of epichlorohydrin on ethyl sodiomalonate, which was previously (*loc. cit.*) converted directly into the amide, has now been isolated as a colourless, odourless oil which boils at 175° under 25 mm. pressure; the *silver* salt has also been prepared from the amide by hydrolysing with sodium hydroxide and precipitating with silver nitrate.

At moderately low temperatures, epichlorohydrin interacts with ethyl sodiomalonate and ethyl sodioacetoacetate in the same manner as ethylene oxide; the first product is probably a chlorohydroxypropyl derivative, but this is at once converted into a lactone by loss of a molecule of alcohol; at higher temperatures, condensation takes place with elimination of sodium chloride, and a similar interaction takes place in the case of ethyl methyl- and ethyl-acetoacetates.

Ethyl δ -chloro- γ -valerolactone- α -carboxylate [lactone of ethyl δ -dichloro- γ -hydroxypropylmalonate], $CH_2Cl \cdot CH \cdot CH_2 \cdot \begin{array}{c} O \\ \diagup \quad \diagdown \\ CO \end{array} > CH \cdot CO_2Et$, prepared from

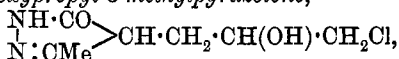
epichlorohydrin and ethyl malonate below 50° , is an oil of sp. gr. 1.274 at 15° which boils at 181° under 12 mm. pressure; the *sodium* salt crystallises from absolute alcohol, and melts and decomposes at 172° ; the diamide has already been described (*loc. cit.*); the *hydrazido-ester*, $C_8H_{15}O_4N_2Cl$, crystallises from alcohol and melts at 129° . *Ethyl*

δ-hydroxy-*γ*-valerolactone-*α*-carboxylate,
$$\text{OH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \begin{array}{c} \text{O} \text{---} \text{CO} \end{array} \text{CH} \cdot \text{CO}_2\text{Et},$$

prepared by the action of alcoholic sodium hydroxide on the chloro-ester, is a colourless syrup which decomposes at about 200° when distilled in a vacuum. *γδ*-Dihydroxypropylmalonamide, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{CO} \cdot \text{NH}_2)_2$, prepared by the action of alcoholic ammonia on the preceding compound, crystallises from dilute alcohol and melts at 140.5°. *Ethyl dichloro-γ-valerolactone-α-carboxylate*, $\text{C}_8\text{H}_{10}\text{O}_4\text{Cl}_2$, prepared by the action of chlorine on the chloro-ester, crystallises from absolute alcohol and melts at 55°; the *bromochloro-ester*, $\text{C}_8\text{H}_{10}\text{O}_4\text{ClBr}$, [is an oil which distils at 180° under 12 mm. pressure.

δ-Chloro-*α*-acetyl-*γ*-valerolactone,
$$\begin{array}{c} \text{CHAc} \cdot \text{CH}_2 \\ \text{CO} \text{---} \text{O} \end{array} \text{CH} \cdot \text{CH}_2\text{Cl},$$
 prepared

from epichlorohydrin and ethyl acetoacetate, is an oil which boils at 163° under 12 mm. pressure. Hydrazine hydrate converts it into 4-*γ*-chloro-*β*-hydroxypropyl-3-methylpyrazolone,

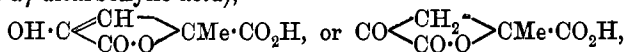


which crystallises in needles from absolute alcohol and melts at 150.5°. *Methyl γδ-dihydroxybutyl ketone*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COMe}$, prepared by warming the lactone with aqueous potassium carbonate, is an oil which is miscible with water and boils at 189—190° under 20 mm. pressure; it combines with 2 mols. of phenylcyanate to a *phenyl-carbamate*, $\text{C}_{20}\text{H}_{22}\text{O}_5\text{N}_2$, which crystallises from alcohol and melts at 136°; sodium amalgam converts the ketone into *αβε-hexanetriol*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot [\text{CH}_2]_2 \cdot \text{CHMe} \cdot \text{OH}$, which is a sweet syrup miscible with water, and distilling at 178° under 12 mm. pressure.

The product of the action of epichlorohydrin on ethyl sodiomethyl-acetoacetate is an oil which boils at 202° under 25 mm. pressure, and is probably acetyloxyethyl-*γ*-valerolactone; ethyl ethylacetoacetate gives an oil boiling at 210° under 25 mm. pressure, which is probably acetyloxyethyl-*γ*-valerolactone.

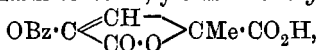
T. M. L.

New Condensation Product from Pyruvic Acid. By LUDWIG WOLFF (*Annalen*, 1901, 317, 1—22. Compare Abstr., 1899, i, 483, 514; and de Jong, this vol., i, 446).—[With WILLY HEROLD].—*α*-Ketovalerolactone-*γ*-carboxylic acid, (*γ*-lactone of *α*-keto-*γ*-hydroxybutane-*αγ*-dicarboxylic acid),



is obtained by allowing pyruvic acid, distilled under 14 mm. pressure, to remain at the ordinary temperature for some weeks and then evaporating under diminished pressure over quicklime; it crystallises from a mixture of ether and benzene in white plates or prisms melting at 116—117°. The acid is hygroscopic and readily dissolves in water, alcohol, or ether, being, however, sparingly soluble in chloroform, benzene, or light petroleum; its aqueous solution reduces Fehling's solution and ammoniacal silver nitrate, develops a red coloration with ferric chloride, and when titrated with sodium hydroxide in cold

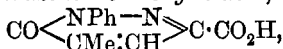
solutions with phenolphthalein as indicator gives numbers corresponding with those for a dibasic acid. In alkaline solutions, the acid is readily reconverted into pyruvic acid. On treating a solution of the compound with lead acetate, a yellow *lead* salt is precipitated having the composition $C_8H_4O_5Pb \cdot 3H_2O$; this substance does not appear to be an immediate derivative of the original ketonic acid, for the acid regenerated from the lead compound gives a phenylhydrazone melting at 182° , whilst the *phenylhydrazone* of α -ketovalerolactone- γ -carboxylic acid obtained by mixing its generators in aqueous solution crystallises from this solvent in yellow needles melting at $197-198^\circ$. The latter phenylhydrazone, when boiled with sodium hydroxide solution, yields a dibasic γ -hydroxy-acid, $C_{12}H_{14}N_2O_5 \cdot 2H_2O$, crystallising in pale yellow needles and melting at 165° . The original ketonic acid, when subjected to the Schotten-Baumann reaction, yields a *benzoyl* derivative,



melting at 118° and developing no coloration with ferric chloride; titration with sodium hydroxide and phenolphthalein indicates that this product is a monobasic acid.

a-iso-Nitrosovalerolactone- γ -carboxylic acid results from the action of hydroxylamine hydrochloride on the ketonic acid; it crystallises from water in lustrous prisms containing $1H_2O$, and melts at $118-119^\circ$. The *isonitroso*-compound does not regenerate hydroxylamine with sodium hydroxide, and develops no coloration with ferric chloride.

1-Phenyl-5-methylpyridazone-3-carboxylic acid,



produced from the γ -hydroxy-acid by heating this substance either alone or with dilute hydrochloric acid, may also be prepared by boiling the phenylhydrazone (m. p. 198°) with sodium hydroxide solution, and treating the product with hot 20 per cent. hydrochloric acid; it melts at $213-214^\circ$ and readily dissolves in alcohol, being sparingly soluble in ether, benzene, or water. 1-Phenyl-5-methylpyridazone, obtained as a by-product in the preceding condensation, crystallises in prisms and melts at $89-90^\circ$; it is isomeric with Ach's 1-phenyl-3-methylpyridazone (Abstr., 1890, i, 71), and like this base gives, after reduction with sodium and alcohol, a red coloration with an acid solution of potassium dichromate.

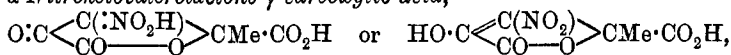
The β -phenylhydrazone, $NHPh \cdot N : C \begin{array}{c} \diagup CMe(CO_2H) \\ \diagdown CO \end{array} > O$, of diketovalerolactone- γ -carboxylic acid, produced by the action of benzenediazonium chloride on a sodium carbonate solution of the ketonic acid, crystallises from glacial acetic acid in brick-red needles and melts at 188° ; it is somewhat sparingly soluble in ether, chloroform, or benzene; its solution in concentrated sulphuric acid develops a deep blue coloration with potassium dichromate.

β -Bromo- α -ketovalerolactone- γ -carboxylic acid, prepared by brominating the ketonic acid in chloroform solution, crystallises from ether and chloroform in white prisms decomposing at 149° ; it is a dibasic acid and develops a red coloration with ferric chloride. When this bromo-acid is treated in aqueous solutions with phenylhydrazine hydrochloride,

two isomeric phenylhydrazones are obtained, together with 1-phenyl-5-methylpyrazole-3-carboxylic acid (m. p. 134°). The *phenylhydrazone*, $\text{NHP}h \cdot \text{N} : \text{C} \begin{smallmatrix} \text{CH} \\ \diagup \text{CO} \cdot \text{O} \end{smallmatrix} \text{CMe}$, of α -ketoangelicalactone separates first from the product of reaction and crystallises from alcohol in yellowish-red needles melting at 128–129°; at this temperature, it is converted into its *isomeride*, $\text{NHP}h \cdot \text{N} : \text{C} \begin{smallmatrix} \text{CH}_2 \\ \diagup \text{CO} \cdot \text{O} \end{smallmatrix} \text{C} : \text{CH}_2$; this substance, which is also produced in the preceding reaction, crystallises in pale yellow needles and melts at 177°. Both isomerides, on boiling in alkaline solution, yield 1-phenyl-5-methylpyrazole-3-carboxylic acid, and their solutions in concentrated sulphuric acid develop violet colorations with potassium dichromate.

3-Methylisooxazole-5-carboxylic acid, $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \text{CH} \\ \diagup \text{N} \cdot \text{O} \end{smallmatrix} \text{CMe}$, results from the action of hydroxylamine hydrochloride on the bromo-acid, and crystallises from boiling water in white prisms or plates melting at 173–174°; the acid readily dissolves in alcohol, hot water, or sodium carbonate solution, and is monobasic.

α -Nitroketovalerolactone- γ -carboxylic acid,



is produced, together with oxalic acid, by slowly adding the ketonic acid to absolute nitric acid cooled to -5° ; the acid readily dissolves in water, alcohol, or ether, but is sparingly soluble in benzene, chloroform, or light petroleum; it crystallises in aggregates of white needles, and melts with decomposition at 152°. In aqueous solution, the acid gradually decomposes, yielding oxalic acid. Two mols. sodium hydroxide neutralise it in cold solution, whereas 3 mols. are required on warming.

G. T. M.

Behaviour of Tertiary Bases towards Methyl Bromomalonate. By EDGAR WEDEKIND (*Ber.*, 1901, 34, 2077–2081. Compare *Zur Stereochemie des fünfwerthigen Stickstoffes*, Leipzig, 1899).—Methyl bromomalonate does not form a quaternary bromide with benzylpiperidine as does the corresponding acetic ester, but loses the elements of hydrogen bromide and yields methyl ethylenetetracarboxylate. This substance forms tabular crystals of the monoclinic system [$a : b : c = 2.2170 : 1 : 1$; $\beta = 83.5^\circ$].

The corresponding ethyl ester is not isomorphous, but forms prismatic crystals of the triclinic system [$a : b : c = 0.5237 : 1 : 1.0854$; $\alpha = 93.18.5'$; $\beta = 117.21.5'$; $\gamma = 95.59.5'$].

The methyl ester is only formed in small quantity from methyl bromomalonate in the ordinary way by the action of sodium ethoxide.

A. H.

Action of Acid Chlorides on Aldehydes in the presence of Zinc Chloride. By MARCEL DESCUDÉ (*Compt. rend.*, 1901, 132, 1567–1569).—Acetyl chloride and trioxymethylene interact energetically in the presence of zinc chloride, giving rise to acetylmethylene chlorohydrin (compare Henry, this Journ., 1873, 1117). When benzoyl chloride is employed, a compound is obtained having the molecular

formula $(C_7H_6O_2)_2$; this substance seems to be a polymeride of benzoic acid.
G. T. M.

New Mode of Decomposition of Bisulphite Derivatives. By PAUL FREUNDLER and L. BUNEL (*Compt. rend.*, 1901, 132, 1338—1340).—When the bisulphite compound of *isovaleraldehyde* (1 mol.) is heated with a solution of sodium nitrite ($\frac{1}{2}$ mol.), the aldehyde is regenerated and nitrilosulphonic acid is produced, the latter being isolated by means of its sparingly soluble potassium salt. The yield of regenerated aldehyde is 90 per cent. of the theoretical, and is somewhat better than that obtained by the action of potassium carbonate.

The method is, however, not applicable to the case of citral, this compound not being completely regenerated from its bisulphite compound under these conditions.
G. T. M.

Bromo-derivatives of Diethyl Ketone. By HERMANN PAULY (*Ber.*, 1901, 34, 1771).—*Bromodiethyl ketone*, $CHMeBr \cdot COEt$, prepared by the action of 1 mol. of bromine on diethyl ketone at about 80° , is a colourless, malodorous oil of sp. gr. 1.37 at 15° , which boils at 157 — 158° under 732 mm. pressure, and does not form a bisulphite compound.

s-**Dibromodiethyl ketone**, $CO(CHMeBr)_2$, prepared in a similar manner by the action of 2 mols. of bromine, has a sp. gr. 1.771 at 18° , boils at 80 — 81° under 12 mm. and at 193 — 195° under 732 mm. pressure, does not form a bisulphite compound, and, like *s*-dichloroacetone, dissolves readily in barium hydroxide solution, apparently with formation of dihydroxydiethyl ketone.
T. M. L.

Cyclic Ketones. By PAVEL IW. PETRENKO-KRITSCHENKO and S. LORDKIPANIDZE (*Ber.*, 1901, 34, 1702—1705. Compare next page).—A series of experiments on the velocity with which ketones of the aliphatic series combine with phenylhydrazine and hydroxylamine respectively to form phenylhydrazones and oximes show that the reactivity of the carbonyl group decreases as the length of the carbon chain increases (compare Menshutkin, *Abstr.*, 1898, i, 119.) Thus, for example, acetone combines with 70 per cent. of phenylhydrazine and 82 per cent. of hydroxylamine when mol. proportions are allowed to interact under the conditions described elsewhere (next page), whilst methyl hexyl ketone combines only with 39 per cent. of the former and 70 per cent. of the latter, and diethyl ketone with 34 and 69 per cent. respectively. In cyclic ketones, such an influence is not exerted; thus ketohexamethylene will combine with 58 per cent. of phenylhydrazine and 86 per cent. of hydroxylamine, and thus closely approaches acetone in activity. Similarly, *p*-diketohexamethylene offers a marked contrast to acetonylacetone, in that it combines with 63 per cent. of phenylhydrazine and 88 per cent. of hydroxylamine, whilst the latter combines with 22 per cent. of phenylhydrazine and 60 per cent. of hydroxylamine under the same conditions. The authors discuss the results on stereochemical grounds, and consider that the cyclic configuration has a more marked

influence on the chemical character of compounds than is generally supposed. K. J. P. O.

Conversion of $\alpha\beta$ -Unsaturated Diketones into α -Diketones. By HERMANN PAULY and HANS VON BERG (*Ber.*, 1901, **34**, 2092—2093).—Ethylideneacetone can be converted into acetylpropionyl [methyl ethyl diketone], $\text{CH}_3\text{Me}\cdot\text{CO}\cdot\text{COMe}$, by a method similar to that employed by Pauly and Lieck (*Abstr.*, 1900, i, 274) for the conversion of mesityl oxide into acetylisobutyryl. For this purpose, the unstable *ethylideneacetone dibromide*, $\text{CHMeBr}\cdot\text{CHBr}\cdot\text{COMe}$, is converted by alcoholic potash into *bromoethylideneacetone*, $\text{CHMe}\cdot\text{CBr}\cdot\text{COMe}$, which boils at 68° under 16 mm. pressure; this is then treated with potassium acetate, and the resulting crude *acetoxylethylideneacetone*, $\text{CHMe}\cdot\text{C}(\text{OAc})\cdot\text{COMe}$, at once hydrolysed with dilute sulphuric acid.

A. H.

α -Diketones. By PAVEL IW. PETRENKO-KRITSCHENKO and E. ELTSCHANINOFF (*Ber.*, 1901, **34**, 1699—1702).— α -Diketones resemble aldehydes, and are distinguished from monoketones by the ability they possess of forming hydrazones with phenylhydrazine hydrochloride. Thus dimethyl diketone reacts immediately at the ordinary temperature with phenylhydrazine hydrochloride, forming a *monophenylhydrazone* melting at 135° , and on heating at 100° , a *diphenylhydrazone* melting at 239° . Methyl ethyl diketone behaves similarly. The reaction between phenylhydrazine and various ketones has been quantitatively studied. Mol. proportions of the ketone and phenylhydrazine in alcoholic solution are mixed and kept for 1 hour at a temperature of 15 — 17° ; the remaining phenylhydrazine is then estimated. With acetone, 74.0 per cent. of the phenylhydrazine had combined, with methyl ethyl diketone, 82.9 per cent., and with acetonylacetone, 30.6 per cent. Similarly, the aromatic α -diketone, benzil, was more reactive than the monoketone, phenyl benzyl ketone. Similar measurements made with cyclic α -diketones show that the ring formation serves still further to intensify the reactivity of the carbonyl groups. Thus under the above-mentioned conditions, benzil combined with 18 per cent. of the phenylhydrazine, acenaphthaquinone with 46.3, phenanthraquinone with 36.8, and retenequinone with 31.3 per cent. Sodium hydrogen sulphite also combines with these cyclic α -diketones, but not with benzil. K. J. P. O.

Acetochloro-dextrose, -galactose, and -lactose. By ZDENKO H. SKRAUP and R. KREMANN (*Monatsh.*, 1901, **22**, 375—384).— γ -Pentacetyldextrose (m. p. 112°) is easily prepared by allowing a mixture of dextrose and excess of acetyl chloride to remain for 8 days at the ordinary temperature (compare Königs and Erwig, *Abstr.*, 1889, 952).

α -Pentacetyldextrose (m. p. 131°) when treated with phosphorus pentachloride and aluminium chloride by the method of von Arlt (this vol., i, 369), either at a low temperature or at 100° , yields an acetylchlorodextrose (hydrose), identical in all respects with the substance obtained from the γ -pentacetate. Acetochlorodextrose is most readily converted into the α -pentacetyldextrose by the action of

dry, finely-powdered silver acetate on its solution in acetic acid. Boiling with acetic acid brings about the same change, but more slowly.

Acetylchlorogalactose, $C_{14}H_{19}O_6Cl$, is obtained by the action of phosphorus pentachloride and aluminium chloride on pentacetylgalactose, and forms white needles melting at 82° (compare Fischer and Armstrong, this vol., i, 189), very soluble in ether, chloroform, alcohol, or benzene. Treated with silver acetate in acetic acid solution, pentacetylgalactose (m. p. 142°) is reformed.

Phenylhydrazine acts readily on both the above acetylchloro-derivatives; phenylhydrazine hydrochloride, and acetylphenylhydrazine were alone isolated.

K. J. P. O.

Galactosamine. By FRIEDRICH N. SCHULZ and FRITZ DITTHORN (*Zeit. physiol. Chem.*, 1901, 32, 428—434).—Galactosamine has been prepared from galactosazone by Fischer's method (Abstr., 1886, 933). Its oxalate was obtained in a crystalline state, but was always mixed with a certain amount of ammonium oxalate. In its properties, it appears to be identical with the galactosamine previously obtained from the glucoproteid of the albuminous gland of the frog (Abstr., 1900, i, 478).

J. J. S.

Refraction of Aqueous Carbohydrate Solutions. II. Muta-rotating Sugars (Disaccharides) and Non-muta-rotating Sugars. By F. STOLLE (*Zeit. Ver. deut. Zuckerind.*, 1901, 469—487. Compare this vol., i, 368).—For aqueous lactose solutions, the following results have been obtained:

| Number of solution. | Ten minutes after solution. | | | Twenty-four hours after solution. | | |
|---------------------|-------------------------------------|-----------------------------------|---------|-------------------------------------|-----------------------------------|---------|
| | Concentration (grams per 100 c.c.). | Sp. gr. at $17.5^\circ/4^\circ$. | n_D . | Concentration (grams per 100 c.c.). | Sp. gr. at $17.5^\circ/4^\circ$. | n_D . |
| 1 | 1.0027 | 1.00204 | 1.33473 | 1.0028 | 1.00218 | 1.33473 |
| 2 | 2.0073 | 1.00617 | 1.33597 | 2.0074 | 1.00626 | 1.33588 |
| 3 | 4.0025 | 1.01357 | 1.33882 | 4.0027 | 1.01361 | 1.33873 |
| 4 | 8.0146 | 1.02842 | 1.34465 | 8.0167 | 1.02869 | 1.34448 |

Thus, with lactose solutions, the alteration in the refractive index is not in the same sense as with the hexoses, an increase in the sp. gr. being accompanied by a decrease in the refractive index. Solutions of the hexoses, with the exception of dextrose, show no variability of the specific refraction (Lorentz and Lorenz formula) with time or concentration, but the values for lactose show a diminution corresponding with the diminution of the refractive index.

The refractive indices of aqueous solutions of sucrose and raffinose have also been determined, the results being given in tables.

Tables are also given showing for solutions of dextrose, lævulose, galactose, sucrose, lactose, and raffinose the values of n_D at 17.5°

corresponding with any concentration of the sugar solution. Where a pure solution of any sugar is available, the measurement of its refractive index serves as a convenient means of determining its concentration; this method is of especial value where only small quantities of liquid can be obtained, a few drops being sufficient for use with Abbe's small direct vision refractometer, whilst with the Pulfrich instrument, which allows of more accurate measurements, about 5 c.c. are required.

T. H. P.

Nitrocelluloses. By GEORG LUNGE and J. BEBIE (*Zeit. angew. Chem.*, 1901, 14, 483—488, 507—515, 537—543 and 561—568. Compare Lunge and Weintraub, *Abstr.*, 1899, i, 559).—The addition of water to the nitrating mixture of sulphuric and nitric acids lessens the percentage of nitrogen contained in the product. With a mixture containing 16.61 to 20.26 per cent. of water, the products obtained at the ordinary temperature are completely soluble in an ether-alcohol mixture, but with a further increase in the percentage of water, the solubility of the product decreases. The authors are not able to confirm Wyss-Naef's statements (*Zeit. angew. Chem.*, 1899, 12, 469). When considerable amounts of water are present and the reaction is continued for some time, the products have the properties of oxy- or perhaps oxynitro-celluloses. When higher temperatures are employed, namely, 40—60°, it is not advisable to prolong the operation, as secondary reactions occur which lower the percentage of nitro-products; the nitration is complete at the end of 15 minutes at 60° with a mixture containing about 19 per cent. of water, and the product is completely soluble. The percentage of water also affects the structure of the product. Mixtures containing less than 15 per cent. of water do not destroy the structure of the cellulose; with mixtures containing 18 per cent. the threads appear to be drawn together, and with still higher percentages the structure becomes completely destroyed, the maximum being obtained with mixtures containing 23—25 per cent. of water.

Increasing the ratio of nitric to sulphuric acid from 1:1 to 1:3 raises the percentage of nitrogen; further increase to 1:4 or 1:5 has but little influence on the percentage of nitrogen.

The formation of oxynitrocelluloses by the action of dilute nitric acid (sp. gr. 1.4) is greatly increased by the addition of sulphuric acid; an addition of 5 per cent. doubles the formation of the oxy-compounds. It appears that a nitrocellulose containing 12.8 per cent. of nitrogen exists in both a soluble and an insoluble modification.

Products containing 13.83 per cent. of nitrogen, and probably corresponding with a dodecanitrate, can be obtained by using a mixture of sulphuric acid 62.95, nitric acid 24.95, and water 12.10 per cent. The product is, however, unstable, and when kept for some months, the percentage of nitrogen sinks to 13.5. With mixtures of sulphuric and fuming nitric acids, the highest nitration product appears to be a nondecanitrocellulose, which can more readily be obtained by a mixture of acids containing 10—12 per cent. of water. With a temperature of 32°, the maximum nitration is reached after 1 hour; an increase in the time favours denitration.

Nitrocelluloses containing 11 to 11.6 per cent. of nitrogen are

soluble in ether-alcohol (3 : 1), also to a certain extent in absolute alcohol, but are insoluble in absolute ether or 95 per cent. alcohol. They are also readily soluble in ether-alcohol 6 : 1, but not so readily in mixtures 9 : 1 or 12 : 1, or in mixtures 1/6 : 1 or 1/12 : 1.

The presence of nitric peroxide in the nitrating mixture does not appear to affect the yield of nitro-products, or yet the stability of the same. Mixtures containing 8—11 per cent. of water yield products which are just as stable as those obtained with mixtures of pure acids.

Celluloses from different sources appear to yield identical products when nitrated in the same way (compare Nettlefold, *Abstr.*, 1887, 792).

Morton-Liebschütz's method of differentiating between hexa- and penta-nitrocelluloses by the aid of polarised light (*Mon. Sci.*, 1891, 119) is worthless, as the same fibre can give both blue and grey colours under slightly different conditions. The method, however, can be used to distinguish between unaltered cellulose which iridesces, and highly nitrated products which give a blue shimmer if the structure of the fibre is still retained.

J. J. S.

An Amine from Trimethylenecarboxylic Acid. By NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 377—383).—Ethyl trimethylenecarboxylate, already prepared by Perkin (*Trans.*, 1885, 47, 815), has the sp. gr. 0.9681 at 15°/4°, and n_D 1.4217 at 15°; the molecular refraction is hence 29.90, the calculated value being 29.47. The

amide of trimethylenecarboxylic acid, $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CO} \cdot \text{NH}_2$, prepared

from the ethyl ester by the action of ammonia, crystallises from water or alcohol in stout, rectangular plates, and from benzene in long needles, melting at 124—125°. By the action of potassium hypobromite, the amide is converted into an *amine* of the composition $\text{C}_3\text{H}_5 \cdot \text{NH}_2$, which boils at 49°, and has a strong ammoniacal odour recalling that of propylamine; it mixes in all proportions with water, and absorbs carbon dioxide from the air, forming a solid carbonate. It has a sp. gr. 0.8254 at 20°/20° and 0.8240 at 20°/4°, and n_D is 1.421 at 20°; the value of the molecular refraction is 17.17, the calculated number being 17.32. The constitution of the amine is as yet unsettled, but it may be represented either by the formula $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{NH}_2$, or by $\text{CH}_2 \cdot \text{CMe} \cdot \text{NH}_2$. The *hydrochloride* separates from alcohol in large, colourless plates melting at 100—101°. By the action of phenylthiocarbimide on a benzene solution of the amine, *phenyltrimethylenylthiocarbimide*, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_3\text{H}_5$, is obtained; it crystallises from alcohol in hexagonal plates melting at 123—123.5°.

T. H. P.

Action of Nitrous Acid on Tetramethylenylmethylamine [ω -Aminomethylcyclobutane]; Methylenetetramethylene Bromide. By NICOLAUS I. DEMJANOFF and M. LUSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 279—283).—The action of nitrous acid on an aqueous solution of ω -aminomethylcyclobutane hydrochloride yields (1) the alcohol obtained by Perkin (*Trans.*, 1901, 79, 329) by reducing

the chloro-anhydride of tetramethylenecarboxylic acid; (2) a hydrocarbon which energetically combines with bromine, giving a *bromide* of the composition $C_5H_8Br_2$; the latter is a colourless liquid boiling at $191-192^\circ$ under 750 mm. pressure, and having an odour recalling, but less sharp than, that of ethylene bromide. T. H. P.

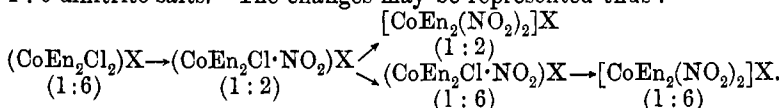
Stereoisomeric Cobalt Compounds. By ALFRED WERNER (*Ber.*, 1901, 34, 1705—1719). — Dichlorodiethylenediaminecobalt salts, $(CoEn_2Cl_2)X$ (where "En" = ethylenediamine) exist in two isomeric forms, distinguished chiefly by physical properties. The "praseo"-salts are green, and the "violeo"-salts are violet, and correspond respectively to the "flavo"- and "croceo"-dinitrotetrammine salts, $[Co(NO_2)_2(NH_3)_4]X$. The author believes that the two series are stereoisomeric, and represents them by the space formulæ previously described (*Abstr.*, 1893, ii, 379). The notation based on this formula represents the "praseo" as 1:6-salts and the "violeo" as 1:2. Similarly, two series of dinitritodiethylenediamine-, $[CoEn_2(NO_2)_2]X$, and chloronitritodiethylenediamine-cobalt salts, $(CoEn_2Cl \cdot NO_2)X$, exist. Both series of salts possess a mol. conductivity which shows that they form in solution two ions; they do not give the reactions of nitrites, and with silver hydroxide their chlorides give strongly alkaline solutions of the base. In the 1:6-series, hydrated or acid salts are frequently formed, whilst in the 1:2-series such salts are not formed. The 1:2-dinitrito-salts are more sparingly soluble, and have a deeper colour than the 1:6-salts. The 1:2-chloronitrito-salts are reddish-orange in colour, whilst the 1:6-salts are yellowish-orange.

The nitrites of both series of dinitrito-salts are obtained by the action of ethylenediamine on potassium cobalt hexanitrite. By the action of sodium nitrite on 1:6-dichlorodiethylenediaminecobalt salts, 60 per cent. of the 1:6-together with 40 per cent. of the 1:2-dinitrito-salts is formed. The 1:2-dichloro-salts under the same conditions yield only the 1:2-dinitrito-salt. The 1:6-salts can also be obtained free from 1:2-salts by oxidation by atmospheric oxygen of a solution of cobaltous chloride containing ethylenediamine and sodium nitrite. The 1:6-dinitritosulphate and iodide can be completely converted into the corresponding 1:2-salts by simply evaporating their aqueous solutions to dryness. The 1:6-nitrate and nitrite, on the other hand, cannot be thus transformed.

By the action of nitric acid on both the 1:2- and 1:6-dinitrito-salts, one of the NO_2 groups becomes displaced by a NO_3 group, and nitratonitrito-compounds, $[CoEn_2(NO_2)NO_3]X$, are obtained. This reaction contrasts with the action of hydrochloric acid on the dinitrito-salts; only the 1:6-salts yield a chloronitrito-salt, whilst the 1:2-salts give a dichloro-salt. The author thinks that as nitric acid behaves with each series in a similar manner, the reaction with hydrochloric acid is not sufficient evidence for the existence of two different constitutions in the two series of salts (compare Jørgensen, *Abstr.*, 1899, ii, 293).

When the 1:6-dichlorodiethylenediaminecobalt chloride is treated with sodium nitrite, the nitrite $(CoEn_2Cl_2)NO_2$ first formed is rapidly transformed, in the absence of excess of nitrous acid, into the chloride

of a chloronitrito-compound, $(\text{CoEn}_2\text{Cl}\cdot\text{NO}_2)\text{Cl}$, a transformation which is accompanied by a change of colour from green to brick-red. This chloronitrito-compound belongs to the 1:2-series, as with sodium nitrite it yields the 1:2-dinitrito-salts. On boiling a solution of the nitrate of this 1:2-chloronitrito-compound, it changes into the nitrate of the 1:6-chloronitrito-series, which with sodium nitrite yields the 1:6-dinitrito-salts. The changes may be represented thus:



From a consideration of these results, the author concludes that the isomerism exhibited by dichloro-, chloronitrito-, and dinitrito-diethylenediaminecobalt salts is of the same order, and is not an isomerism due to difference of constitution, but to difference of spacial configuration, and most nearly allied to "cis-trans" isomerism. K. J. P. O.

Stereoisomeric Dinitritodiethylenediamine Cobalt Salts, $[\text{CoEn}_2(\text{NO}_2)_2]\text{X}$. By ALFRED WERNER and ED. HUMPHREY (*Ber.*, 1901, **34**, 1719—1732. Compare preceding abstract).—A mixture of the nitrites of the 1:2- and the 1:6-dinitritodiethylenediamine compounds is obtained when potassium cobalt hexanitrite, $\text{Co}(\text{NO}_2)_6\text{K}_3$, and ethylenediamine are warmed together in aqueous solution.

1:2-Dinitritodiethylenediaminecobalt nitrite, $[\text{CoEn}_2(\text{NO}_2)_2]\text{NO}_2$, forms 80 per cent. of the mixed salts, and separates first on fractional crystallisation. It crystallises in dark brown or black prisms and also in light brown needles. The *nitrate* is prepared by the action of nitric acid on the preceding salt, and crystallises in long, lustrous, four-sided prisms of a light brown colour which exhibit dichroism and are very insoluble in water. It explodes at 200° , and when evaporated with nitric acid, it yields a mixture of a nitritonitrato-, $[\text{CoEn}_2(\text{NO}_2)\cdot\text{NO}_3]\text{NO}_3$, and a dinitrato-diethylenediaminecobalt nitrate, $[\text{CoEn}_2(\text{NO}_3)_2]\text{NO}_3$. With solutions of various salts, this 1:2-nitrate gives a number of precipitates, which serve to distinguish it from the isomeric 1:6-salt. The *chloride* prepared from the nitrite by treating it with hydrochloric acid in the presence of carbamide, crystallises in broad, brown plates, which are converted into 1:6-dichlorodiethylenediaminecobalt chloride by hydrochloric acid. The *bromide* is prepared by neutralising with hydrobromic acid a solution of the base which is obtained by shaking up a cold solution of the chloride with moist silver hydroxide. This salt crystallises in dark brown plates resembling the chloride. The *iodide*, prepared in a similar manner, forms reddish-brown prisms; the *sulphate*, prepared from the nitrate and ammonium sulphate, crystallises in silky, light brown, very insoluble needles. Determinations of the electrical conductivity of the above salts gave values for μ varying from 90—100 at a dilution $v=1024$. The *platinichloride* is very insoluble, and crystallises in microscopic prisms terminated by pyramids; the *platinochloride* forms orange leaves, the *aurichloride*, golden-brown needles.

1:6-Dinitritodiethylenediaminecobalt nitrite, $[\text{CoEn}_2(\text{NO}_2)_2]\text{NO}_2\cdot 2\text{H}_2\text{O}$, is separated from its isomeride by fractional crystallisation, and

crystallises in brownish-yellow rhombs which very readily effloresce. The *nitrate* forms large plates which are very insoluble; with nitric acid, it yields red nitritonitrato-salts. The *chloride*, with $2\text{H}_2\text{O}$, prepared from the base and hydrochloric acid, or from the iodide and silver chloride, crystallises in pale yellow, four-sided prisms, which effloresce, and are converted by hydrochloric acid into chloronitrito-salts. For the foregoing salts, μ has the value 90—100 for $v=1024$. The *bromide* crystallises with $2\text{H}_2\text{O}$ in light brown prisms, and is prepared from the iodide. The *iodide*, prepared from the nitrate and potassium iodide, forms light brown plates, little soluble in water. The *sulphate* could not be prepared, as in evaporation of its solutions it transformed into the isomeric 1:2-salt. The *platinichloride* crystallises in pale yellow needles, and the *platinochloride* in brown plates.

K. J. P. O.

1:6-Chloronitritodiethylenediaminecobalt Salts, $(\text{CoEn}_2\text{Cl}\cdot\text{NO}_2)_\text{X}$. By ALFRED WERNER (*Ber.*, 1901, 34, 1733—1738).—A pure neutral solution of 1:6-dichlorodiethylenediaminecobalt chloride (prepared by Jörgensen's method, *Abstr.*, 1889, 351) is stirred with a rod of sodium nitrite. The colour changes from green to red, and bright red crystals of the 1:2-chloronitrito-chloride separate; the latter is converted into the nitrate by the action of nitric acid.

1:6-Chloronitritodiethylenediaminecobalt *nitrate*, prepared by boiling an aqueous solution of the 1:2-chloronitrito-nitrate, crystallises in red, four-sided crystals. With nitric acid, it forms an *acid salt*, a red, lustrous, crystalline powder which is decomposed by water into nitric acid, and the normal salt, the same change occurring when it is kept in a desiccator. The *iodide*, prepared from the nitrate and potassium iodide, forms brownish-orange plates; the *chloride*, which crystallises with $1\text{H}_2\text{O}$, forms red plates; the *thiocyanate* crystallises in sparingly soluble needles.

K. J. P. O.

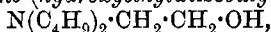
1:2-Chloronitritodiethylenediaminecobalt Compounds. By ALFRED WERNER and L. GERB (*Ber.*, 1901, 34, 1739—1745. Compare previous abstract).—1:2-Chloronitritodiethylenediaminecobalt *chloride*, $(\text{CoEn}_2\text{Cl}\cdot\text{NO}_2)_2\text{Cl}$, prepared as previously described (*loc. cit.*) from 1:6-dichlorodiethylenediamine nitrite, crystallises in light red, lustrous needles, which are converted by concentrated hydrochloric acid into 1:6-dichlorodiethylenediaminecobalt chloride. The *nitrate*, prepared from the chloride, forms red leaves sparingly soluble in water, and decomposed in aqueous solution into the 1:6-isomeride. The *acid sulphate*, prepared from the chloride and concentrated sulphuric acid, forms a dark red, amorphous powder insoluble in cold water and decomposed by hot water. The *nitrite* crystallises in microscopic prisms, which are converted in aqueous solution into the dinitritodiethylenediaminecobalt chloride. The *iodide* forms a red, crystalline precipitate; the *bromide* resembles the iodide; both are changed by heating with water. The *thiocyanate* crystallises in brick-red prisms which readily transform into the thiocyanonitrito-salt, $[\text{CoEn}_2(\text{NO}_2)_2\cdot\text{SCN}]\text{Cl}$.

By the action of silver nitrate on the chloride just described, the *nitrate* of a nitratonitrito-compound, $[\text{CoEn}(\text{NO}_2)_2\cdot\text{NO}_3]\text{NO}_3$, is obtained as a pale yellow, crystalline precipitate. The nitrate of the 1:2-

chloronitrito-compound, both with sodium and silver nitrite, yields a 1 : 2-dinitrito-salt.
K. J. P. O.

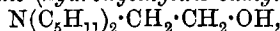
Alcohol Bases. By HERMANN MATTHES (*Annalen*, 1901, 316, 311—317. Compare this vol., i, 259).—*Ethanoldipropylamine* (*hydroxyethyldipropylamine*), $\text{NPr}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, is a colourless oil boiling at $195\text{--}196^\circ$ under 758 mm. pressure, obtained by mixing dipropylamine with ethylene oxide in the presence of water; it volatilises in steam and is strongly basic, having an ammoniacal odour; it has a sp. gr. 0.8576 at $20^\circ/0^\circ$, n_D 1.4402 at 20° , and molecular refraction 44.566, the theoretical value for this constant being 44.494. The *picrolonate*, $\text{C}_8\text{H}_{19}\text{NO}$, $\text{C}_{10}\text{H}_{21}\text{NO}_5\text{N}_4$, and *picrate* melt respectively at $128\text{--}130^\circ$ and $80\text{--}82^\circ$.

Ethanoldiisobutylamine (*hydroxyethyldiisobutylamine*),



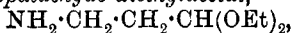
obtained in a similar manner to the preceding base, is a colourless oil boiling at $213\text{--}214^\circ$ under 754 mm. pressure; it has a sp. gr. 0.8407 at $20^\circ/4^\circ$ and n_D 1.4355 at 20° , the molecular refraction calculated from the refractive index being 53.753, whilst the theoretical value is 53.70. The *picrolonate* and *picrate* are yellow, crystalline salts melting respectively at $134\text{--}135^\circ$ and $123\text{--}125^\circ$; the *aurichloride* is somewhat insoluble in cold water or alcohol, it separates at first as an oil, and then solidifies in the cold to yellow, rhombic crystals melting at $86\text{--}88^\circ$.

Ethanoldiisoamylamine (*hydroxyethyldiisoamylamine*),

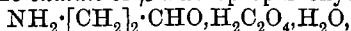


prepared by heating its generators in sealed tubes at 150° , is a colourless oil having an odour resembling that of amyl alcohol; it boils at $247\text{--}248^\circ$ under 748 mm. pressure, and has a sp. gr. 0.8492 at $20^\circ/4^\circ$ and n_D 1.4435 at 20° , the experimentally determined and calculated values of the molecular rotation being 62.815 and 62.906. The *picrolonate* crystallises in hexagonal leaflets melting at 88° ; the *picrate* is oily. These bases are sparingly soluble in water, the solubility diminishing as the homologous series is ascended; their aqueous solutions have a strongly alkaline reaction; they readily dissolve in the ordinary organic solvents.
G. T. M.

Aminoacetals and Aminoaldehydes. By ALFRED WOHL (*Ber.*, 1901, 34, 1914—1924).—[With M. WOHLBERG.]—When β -chloropropaldehyde diethylacetal is treated with alcoholic ammonia, a mixture of β -aminopropaldehyde diethylacetal,

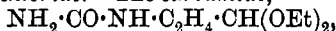


and the secondary base, $\text{NH}[\text{C}_2\text{H}_4 \cdot \text{CH}(\text{OEt})_2]_2$, is obtained; the former is a colourless, basic liquid having a sp. gr. 0.9359 at 17° , boils at 80° (corr.) under 18 mm. pressure, and when treated with oxalic acid yields the crystalline *oxalate* of β -aminopropaldehyde,



which, when anhydrous, melts at 98° . The *platinichloride* of the aminoaldehyde is soluble in water and insoluble in alcohol. Phenylthiocarbimide combines with the acetal and yields the *thiocarbamide*, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_2\text{H}_4 \cdot \text{CH}(\text{OEt})_2$, which forms colourless crystals, melts at 85° (corr.), and when treated with concentrated hydrochloric acid

yields *phenyldihydropyrimidyl mercaptan*, $\text{CH} \begin{smallmatrix} \text{CH} \cdot \text{NPh} \\ \text{CH}_2 - \text{N} \end{smallmatrix} \text{C} \cdot \text{SH}$; this crystallises from water, melts at 151° , is acid in character, but forms a crystalline *platinichloride*. The *carbamide*,



obtained by treating a neutralised solution of the aminoacetal with potassium cyanate, forms deliquescent crystals melting at 61° . The *benzoyl* derivative of the aminoacetal is a pale yellow syrup and, when

treated with oxalic acid, forms *phenyl-1:3-oxazine*, $\text{O} \begin{smallmatrix} \text{CPh} : \text{N} \\ \text{CH} : \text{CH} \end{smallmatrix} \text{CH}_2$

which crystallises from alcohol and melts at 171° ; the *acetyl* derivative is a yellow oil of sp. gr. 0.9937 at 17° ; the *benzylidene* derivative, obtained by the condensation of the aminoacetal with benzaldehyde, is a colourless oil of sp. gr. 0.9878 at 17° , boils at 157° under 11 mm. pressure and, when reduced, yields the *benzyl* derivative, which is a yellowish oil of sp. gr. 0.9799 at 17° , boils at 156° under 14 mm. pressure and, when treated with concentrated hydrochloric acid, yields

the *hydrochloride* of phenyldihydropyrrole, $\begin{smallmatrix} \text{CH} - \text{CH}_2 \\ | \quad \quad | \\ \text{CH} \cdot \text{CHPh} \end{smallmatrix} \text{NH} \cdot \text{HCl}$, which melts at 240° (corr.).

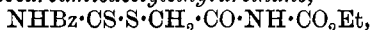
[With K. SCHÄFER.]—*β-Cyanopropaldehyde diethylacetal*, obtained by the action of potassium cyanide on the corresponding chloro-compound, is an oil boiling at 106° under 45 mm. pressure and when reduced by sodium in alcoholic solution yields *γ-aminobutyraldehyde diethylacetal*, which is a colourless basic oil boiling at 196° or at 96° under 21 mm. pressure.

R. H. P.

Action of Alkyl Thiocyanates and Alkyl *iso*Thiocyanates [Thiocarbimides] with Thiol Acids. By HENRY L. WHEELER and HENRY F. MERRIAM (*J. Amer. Chem. Soc.*, 1901, 23, 283—299).—By the action of thioacetic acid on ethyl thiocyanate, Chanlaroff (*Abstr.*, 1883, 39) obtained ethyl acetyldithiocarbamate. The authors have confirmed this, and have found that acyldithiocarbamates may be readily prepared by warming a benzene solution of the thiocyanate for a few hours with thioacetic or thiobenzoic acid. The compounds thus obtained are yellow, well crystallised substances, readily soluble in hot alcohol, and sparingly in cold; they dissolve in aqueous alkali, and are reprecipitated by carbon dioxide. *Methyl acetyldithiocarbamate*, $\text{NHAc} \cdot \text{CS} \cdot \text{SMe}$, crystallises in long, slender, bright yellow prisms, and melts at 119° . By the action of ethyl bromide and sodium ethoxide on the corresponding ethyl ester, *ethyl acetylaminodithiocarbonate*, $\text{NAc} \cdot \text{O}(\text{SEt})_2$, is obtained as a colourless oil which boils at 142° . *Propyl acetyldithiocarbamate* crystallises in brilliant yellow plates or prisms, and melts at 78° . *Cetyl thiocyanate*, $\text{C}_{16}\text{H}_{32} \cdot \text{SCN}$, obtained by the action of cetyl iodide on potassium thiocyanate, boils at 242 – 249° under 30 mm. and at 222 – 227° under 13 mm. pressure, and, on cooling, solidifies as a white wax which melts at 15 – 15.5° . *Cetyl acetyldithiocarbamate* crystallises in slender needles, and melts at 89 – 90° ; it dissolves in dilute alkali with formation of the sodium salt, which separates in thin, colourless plates. *Benzyl acetyldithiocarbamate* crystallises in bright yellow plates and melts at 136° .

Methyl benzoyldithiocarbamate forms slender yellow needles and melts at 135° . The corresponding *ethyl* ester crystallises in stout, yellow prisms and melts at 84° . *Methyl benzoyliminodithiocarbonate*, $\text{NBz}\cdot\text{C}(\text{SMe})_2$, crystallises in long, colourless prisms, and melts at 46° , whilst the *ethyl* ester is obtained as an oil which boils at $220\text{--}221^{\circ}$ under 17 mm. pressure. When the methyl ester is dissolved in excess of alcoholic ammonia and left for 2 days, mercaptan separates, and *benzoyl- ψ -methylthiocarbamide*, $\text{NBz}\cdot\text{C}(\text{SMe})\cdot\text{NH}_2$, is produced, melting at $111\text{--}112^{\circ}$. *Benzoyl- ψ -methylphenylthiocarbamide*, $\text{NBz}\cdot\text{C}(\text{SMe})\cdot\text{NHPh}$, obtained by warming the methyl benzoyliminodithiocarbonate with aniline, forms thin, colourless plates and melts at $104\text{--}105^{\circ}$. *Benzoyl- ψ -ethylphenylthiocarbamide* crystallises in long, colourless prisms and melts at $87\text{--}88^{\circ}$. *Propyl benzoyldithiocarbamate* crystallises in bright yellow prisms and melts at 77° . The *isobutyl* ester forms golden yellow needles and melts at $80\text{--}81^{\circ}$. The *cetyl* ester crystallises in bright yellow plates and melts at $63\text{--}64^{\circ}$. Benzyl thiocyanate melts at $43\text{--}43.5^{\circ}$. *Benzyl benzoyldithiocarbamate* crystallises in long, yellow needles, melts at 108° , and yields a sodium salt which separates in thin, colourless plates.

If phenyl thiocyanate is heated with thiobenzoic acid, phenyl thiolbenzoate is produced. Phenyl thiocyanate is not readily converted into phenylthiocarbimide; if left for 4 weeks at $34\text{--}36^{\circ}$, it remains practically unaltered. When 2:4-dinitrophenyl thiocyanate is heated with thioacetic acid, tetranitrophenyl disulphide is obtained, whilst by the action of thiobenzoic acid, benzoyldinitrophenyl mercaptan is produced, which is converted by alkalis into tetranitrophenyl disulphide. Thiocyanacetylethylurethane reacts with thiobenzoic acid with formation of *benzoyldithiocarbamicacetyethylethylurethane*,



which crystallises in thin, golden-yellow plates and melts at 159° . By the action of thiobenzoic acid on methyl thiocyanacetate, *methyl benzoyldithiocarbamicacetate*, $\text{NHBz}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, is obtained, which crystallises in bright yellow prisms and melts at 118° . When thiocyanacetamide is heated with thiobenzoic acid, hydrogen cyanide, benzoyl disulphide, and a black, tarry substance are produced. *Benzoylthioglycollamide*, $\text{SBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, obtained from potassium thiolbenzoate and chloroacetamide, crystallises from hot water in long, colourless prisms and melts at $119\text{--}120^{\circ}$. When thiocyanomethylacetanilide is heated with thiobenzoic acid, *benzoyldithiocarbamicmethylacetanilide*, $\text{NHBz}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NMePh}$, is obtained in yellow prisms melting at 152° .

Allylthiocarbimide and thiobenzoic acid react with formation of carbon disulphide and allylbenzamide, and by the action of thiobenzoic acid on phenylthiocarbimide, carbon disulphide and benzanilide are produced; similarly, thioacetic acid reacts with phenylthiocarbimide to form acetanilide. 2-Chloroallylbenzamide, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CCl}\cdot\text{CH}_2$, obtained by the action of thiobenzoic acid on α -chloroallylthiocarbimide, crystallises in long, colourless prisms and melts at 95° . Benzoylthiocarbimide reacts with thiobenzoic acid with formation of dibenzamide.

Ethyl selenocyanate, EtSeCN , obtained by the action of ethyl

bromide on potassium selenocyanate, is a pale yellow oil of unpleasant odour, which boils at 172° under 741 mm. pressure; it reacts with thiobenzoic acid, but the products have not been investigated.

E. G.

Thiocyanogen, the so-called ψ -Thiocyanogen and the Yellow Colouring Matters obtained from Thiocyanates. By ALWIN GOLDBERG (*J. pr. Chem.*, 1901, [ii], 63, 465—495).—After considering the previous work on the subject, of which a summary is given, the author comes to the conclusion that thiocyanogen, $(\text{CNS})_x$, has not been obtained in a pure state.

The author finds that the ψ -thiocyanogen, obtained by oxidising thiocyanates by potassium chlorate and hydrochloric acid, becomes changed into the dye "canarin," when treated with alkalis. This dye, prepared from its sodium salt, has the formula $\text{C}_8\text{H}_6\text{ON}_8\text{S}_7$, and represents about half the ψ -thiocyanogen from which it is formed.

The same ψ -thiocyanogen and dye are obtained by the action of excess of chlorine on thiocyanates. The investigation of the action of bromine on potassium thiocyanate shows that the best yield of ψ -thiocyanogen is obtained when molecular quantities of thiocyanate and bromine are employed. At the same time, oxidation to sulphate and cyanic acid always takes place to a considerable extent. Perthiocyanic acid is also formed in the reaction. Nitric acid in various proportions converts about 27 per cent. of potassium thiocyanate into ψ -thiocyanogen; considerable oxidation to sulphuric acid, etc., occurs, and a little perthiocyanic acid is formed.

K. J. P. O.

A peculiar Double Cyanide. By OTTO HERTING (*Zeit. angew. Chem.*, 1901, 14, 585—586).—See this vol., ii, 534.

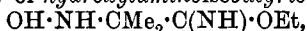
Preparation of Fulminates. By FRANCESCO ANGELICO (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 476—478).—In place of the old method, which causes a copious evolution of an explosive mixture consisting mainly of ethyl nitrite and nitrate, the author gives the following for the preparation of mercury fulminate. A concentrated aqueous solution of malonic acid is added to a solution of mercury in excess of dilute nitric acid. The reaction generally begins spontaneously if the liquid be hot, but if not, the addition of a few drops of sodium nitrite solution causes an evolution of carbon dioxide, which gradually increases until it becomes tumultuous. Towards the end of the action, mercury fulminate separates as a white, crystalline powder which can be recrystallised from water. The first phase of the reaction is probably the formation of *isonitrosomalonic acid*, which passes successively into *isonitromalonic acid*, *isonitroacetic acid*, and *isonitromethane*, which then loses water, giving the oxime of carbonic oxide which Nef regards as fulminic acid. When cyanoacetic acid is used in place of the malonic acid, an insoluble double mercury salt, the constitution of which is not yet decided, is obtained.

T. H. P.

Nitrosoisobutyronitrile and its Derivatives. By OSCAR PILOTY and B. GRAF SCHWERIN (*Ber.*, 1901, 34, 1863—1870. Compare Abstr., 1898, i, 616).—Nitrosoisobutyronitrile is readily obtained by the oxidation of the corresponding hydroxylamino-compound with chlorine

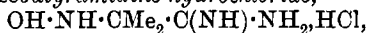
water at 0°. When kept, it gradually changes to a blue liquid which rapidly decomposes into nitrosoisobutyronitrile, a compound $C_{12}H_{18}ON_4$, and nitric oxide. When treated with concentrated hydrochloric acid at 0°, it is converted into nitrosoisobutyramide, melting at 158°. The same product is more readily obtained by the oxidation of the hydroxylamino-amide. Nitrosoisobutyramide, $NO_2 \cdot CMe_2 \cdot CO \cdot NH_2$, is obtained when the nitro-nitrile is shaken with hydrochloric acid saturated at 0°; it forms glistening plates, melts at 117—118°, and is only moderately soluble in ether.

The ethylimino-ether of hydroxylaminoisobutyric acid,



in the form of its hydrochloride (with 2HCl), is obtained by passing hydrogen chloride into an alcoholic solution of the hydroxylamino-nitrile at 0°; it melts and decomposes at about 108° and is somewhat unstable. When oxidised with chlorine and water at 0°, it yields ethyl nitrosoisobutyrate in the form of colourless crystals melting at 89° to a blue oil. The oil previously described by Gomberg (Abstr., 1898, i, 354) as the nitroso-ester is more probably the ester of hydroxylaminoisobutyric acid.

Hydroxylaminoisobutyramidine hydrochloride,



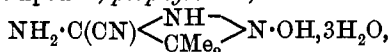
melts and decomposes at 154°, dissolves readily in water, and on oxidation with chlorine water yields nitrosoisobutyramidine hydrochloride, which melts and decomposes at 161°, is only sparingly soluble in cold water, and gives a precipitate with sulphuric acid. Other oxidising agents convert the hydroxylaminoamidine into different products.

J. J. S.

Existence of Derivatives of Quadrivalent Nitrogen. I

By OSCAR PILOTY and B. GRAF SCHWERIN (*Ber.*, 1901, 34, 1870—1887).—Numerous experiments have been made in order to synthesise aliphatic azo-compounds by the condensation of amino-compounds with nitroso-derivatives, but so far without success. Nitrosoisobutyronitrile and aniline in presence of acetic acid yield aminoazobenzene, which is undoubtedly formed by the elimination of nitrous acid from the nitroso-compound.

An aqueous solution of potassium cyanide reacts with nitrosoisobutyramidine hydrochloride (compare preceding abstract) at 30° to 50°, yielding a basic compound, porphyrexine,



which crystallises in compact, colourless prisms sintering at 110°. The anhydrous compound obtained by heating at 130° melts and decomposes at 248—250°; it crystallises from alcohol in glistening, felted needles containing 1EtOH, but is practically insoluble in benzene or light petroleum, and the anhydrous compound is strongly hygroscopic. The hydrochloride, $C_5H_{10}ON_4 \cdot HCl$, crystallises in rhombic plates, melts and decomposes at 272°, and is readily soluble in water. The oxalate $(C_5H_{10}ON_4)_2 \cdot H_2C_2O_4 \cdot 2H_2O$, forms prismatic needles melting and decomposing at 254°; the sulphate melts at 289°. When heated with hydrochloric acid at 100°, porphyrexine yields a compound,

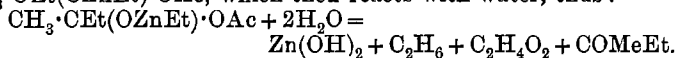
$C_{10}H_{20}O_4N_6Cl_2$, probably the hydrochloride of the anhydride of an amino-acid. It crystallises in prisms, melts at about 192° , and is readily soluble in water or alcohol.

Hydrogen sulphide acts on porphyrexine suspended in alcohol yielding a compound $C_{10}H_{18}O_2N_6S_2$, probably a sulphur analogue of the anhydride formed by the action of hydrochloric acid. It crystallises from hot water in yellowish, rhombic prisms melting and decomposing at 231° , and is insoluble in most organic solvents with the exception of alcohol.

When reduced with sodium amalgam, porphyrexine is converted into a syrup, and when oxidised with potassium permanganate, or, still better, with potassium ferricyanide in the presence of alkali, it yields a basic compound, *porphyrexide*, $C_5H_9ON_4$, which crystallises in brick-red, prismatic plates melting and decomposing at 157° ; this is only sparingly soluble in cold water, more readily in hot alcohol, but gradually undergoes decomposition. It has strong oxidising properties, reacting with hydrogen sulphide or sulphur dioxide, and regenerating porphyrexine; it also oxidises hydrochloric acid, or acidified potassium iodide. It forms salts with both acids and bases. The *nitrate*, $C_5H_9ON_4 \cdot HNO_3$, crystallises in lemon-yellow plates melting and decomposing at 127° . The *sodium* salt, $C_5H_8ON_4Na \cdot H_2O$, forms deep violet coloured crystals melting and decomposing at about 100° , and readily soluble in both water and alcohol. It is thought probable that this oxidation product has the formula $NH_2 \cdot C(CN) \langle \begin{smallmatrix} NH \\ CMe_2 \end{smallmatrix} \rangle N : O$, and contains a quadrivalent nitrogen atom (compare Hantzsch and Semple, Abstr., 1896, ii, 95).
J. J. S.

Iminodithiocarbonic Esters, $RN : C(SR')_2$. By MARCEL DELÉPINE (*Compt. rend.*, 1901, 132, 1416—1418).—Diethyl- and diisobutylformocarbothialdines with methyl iodide yield respectively the compounds $NEt : C(SMe)_2$ and $C_4H_9 : N : C(SMe)_2$, whilst with ethyl iodide dimethylformocarbothialdine yields the compound $NMe : C(SEt)_2$. The substituted iminodithiocarbonic esters are also readily obtained by the successive action of carbon disulphide and an alkyl iodide on a primary amine of the methane series. When oxidised with nitric acid, they yield a sulphonic acid and an amine, the central carbon atom being eliminated; when reduced by sodium in presence of alcohol, they yield a diamine and a sodium mercaptide. They also react with salts of mercury, silver, or platinum.
C. H. B.

Action of Zinc Ethyl on Anhydrides of Organic Acids, Oxides, and Lactones. By EMERICH GRANICHSTÄDTEN and FRIEDRICH WERNER (*Monatsh.*, 1901, 32, 315—334).—It is shown that acetic anhydride and zinc ethyl first form an additive product, $CH_3 \cdot C(Et)(OZnEt) \cdot OAc$, which then reacts with water, thus:



Estimation of the ethane, acetic acid, and methyl ethyl ketone formed proved the correctness of this equation (compare Saytzeff, *Zeit. f. Chem.*, 1870, 107).

Butyric anhydride and zinc ethyl yield an analogous additive pro-

duct, which when decomposed by water gives ethane, ethyl propyl ketone, and butyric acid. Zinc ethyl has no action on the oxides, ethylene oxide, the oxides from *isobutylene glycol* (Franke, Abstr., 1896, i, 404), diphenylene oxide, paraldehyde, &c.

With valerolactone, zinc ethyl reacts at a temperature of 80°, ethane is evolved, and from the solid residue, by the action of dilute sulphuric acid, an oil was obtained which proved to be dimethyloxetone (Fittig and Rasch, Abstr., 1890, 867 and 868). It is shown that the zinc ethyl has effected the condensation of two molecules of valerolactone, with elimination of water; the divalolactone thus formed is converted by water and zinc hydroxide or by sodium hydroxide into divalonic acid, which by boiling with dilute sulphuric acid yields dimethyloxetone (compare Fittig, *loc. cit.*).

Butyrolactone and zinc ethyl react when heated, with evolution of ethane; from the solid residue, by boiling with sulphuric acid until the evolution of carbon dioxide ceased, oxetone was obtained.

Phthalide and zinc ethyl do not react, even when heated at 170° for days.

K. J. P. O.

***o*-isoPropyltoluene** [*o*-Methylisopropylbenzene]. By H. SPRINKMEYER (*Ber.*, 1901, 34, 1950—1954).—*o*-Methylisopropylbenzene, obtained by the action of sodium on a mixture of *o*-bromocumene and methyl iodide, is a colourless liquid boiling at 157°, has a sp. gr. 0.8582 at 18°/18° and n_D 1.495; when oxidised with potassium permanganate, it yields dimethylphthalide. When treated with fuming sulphuric acid at 50°, at least two *monosulphonic acids* are formed; one of these forms sparingly soluble salts, of which the *barium* (with H_2O), the *lead* (with $2H_2O$), the *copper* (with $8H_2O$), and the *potassium* (with $2H_2O$) salts are described, and a *sulphonamide*, which crystallises in clusters of needles and melts at 90°; the other acid forms more soluble salts and a *sulphonamide*, which crystallises in lustrous leaflets and melts at 105°.

R. H. P.

Constitution of a Bromo-derivative of *iso*Butylbenzene. By F. BODROUX (*Bull. Soc. Chim.*, 1901, [iii], 25, 628—629).—The substance, $C_{10}H_9Br$, obtained by the action of an excess of bromine, on a mixture of *isobutylbenzene* and aluminium bromide has probably the constitution represented by the formula $C_6Br_5 \cdot CHBr \cdot CMeBr \cdot CHBr_2$.

T. M. L.

Alkylated Aminobenzenesulphonic Acids and *m*-Aminophenols. By ROBERT GNEHM and TH. SCHEUTZ (*J. pr. Chem.*, 1901, [ii], 63, 405—427).—The alkylation of *m*-aminobenzenesulphonic acid or of the salts of *m*-acetylaminobenzenesulphonic acid was not found possible. *Barium m*-acetylaminobenzenesulphonate, prepared by acetylating barium *m*-aminobenzenesulphonate, crystallises, with $2H_2O$, in colourless needles; the *sodium* salt, with $2H_2O$, forms needles melting at 184—185°. The free acid could not be isolated from the salts.

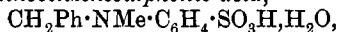
m-Methylaminobenzenesulphonic acid, $NHMe \cdot C_6H_4 \cdot SO_3H$, prepared by sulphonating methylaniline, crystallises in long needles decomposing at 285—290°. The *sodium* and *barium* salts are anhydrous crystalline powders. An isomeric acid is obtained in the sulphonation of methylaniline if the temperature is allowed to rise; above 150°, it is alone

formed; it crystallises in large, anhydrous plates decomposing at 244° . The *sodium* salt crystallises, with $3\text{H}_2\text{O}$, in white plates; the *barium* salt forms crystals with H_2O .

m-Ethylaminobenzenesulphonic acid, prepared by sulphonating ethylaniline, crystallises in needles decomposing at 294° , and having the affinity constant $K=0.0159$. The *sodium* salt crystallises in white leaflets with $2\text{H}_2\text{O}$; the *barium* salt forms anhydrous crystals.

m-Ethylaminoazobenzenesulphonic acid, prepared by the action of benzenediazonium salts on the sulphonic acid, crystallises in microscopic, yellow needles melting at 165° . Another ethylaminobenzenesulphonic acid is also obtained in sulphonating ethylaniline, and crystallises in anhydrous plates decomposing at 258° , and having the affinity constant $K=0.0125$. A consideration of the affinity constants of this acid and of the three aminobenzenesulphonic acids leads to the conclusion that it and its methyl analogue are both para-derivatives, whilst the methylaminobenzenesulphonic acid obtained by Mundelius (*Ber.*, 1874, 7, 1350) is an ortho-derivative. The *sodium* salt, $\text{NHEt}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}\cdot 3\text{H}_2\text{O}$, crystallises in plates or prisms; the *barium* and *silver* salts each crystallise, with H_2O , in plates.

m-Benzylmethylaminobenzenesulphonic acid,



crystallises in needles; the *sodium* salt, obtained by heating benzyl chloride with sodium *m*-methylaminobenzenesulphonate in the presence of sodium hydroxide, crystallises in small leaflets or needles with $2\text{H}_2\text{O}$; the *barium* salt, with $3\text{H}_2\text{O}$, forms white scales.

Sodium benzylethylaminobenzenesulphonate, obtained in like manner to the analogous methyl derivative, is anhydrous; the *barium* salt crystallises in prisms with $3\text{H}_2\text{O}$.

m-Methylaminophenol, $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, obtained by the action of molten potassium hydroxide on the sulphonic acid, is a solid which boils at 170° under 12 mm. pressure. *m*-Ethylaminophenol forms a white, crystalline powder melting at 62° and boiling at 176° under 12 mm. pressure. *m*-Benzylethylaminophenol is a solid.

With phthalic anhydride, *m*-ethylaminophenol yields a phthalein, diethylrhodamine, which forms the main part of the Rhodamine 6 G. of commerce. The *phthalein* of *m*-benzylethylaminophenol is a reddish-brown powder the carmine-red solutions of which exhibit a yellow fluorescence.

On nitrating benzylethylaniline at 0° in the presence of sulphuric acid, a *nitro*-derivative is obtained which forms red crystals. The *nitro*-group is in the para-position, as the base obtained on reduction does not give a rhodamine with phthalic anhydride, and gives a blue colour with ferric chloride.

K. J. P. O.

Derivatives of 2-Chloronaphthalene. By KARL SCHEID (*Ber.*, 1901, 34, 1813—1818).—By nitration in acetic acid solution, 2-chloronaphthalene is converted into 2:8-chloronitronaphthalene (Armstrong and Wynne, *Proc.*, 1893, 9, 166) which is accompanied by a number of higher *nitro*-products. When the 2-chloronaphthalene is directly treated with nitric acid or dissolved in sulphuric acid and then treated with nitric acid, during the addition of which it is cooled, the chief

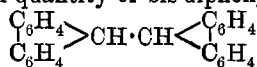
product is 2-chloro-1:6-dinitronaphthalene, which crystallises in short, yellow needles melting at 174°. The chlorine atom can very readily be replaced and the compound is converted by alcoholic ammonia into a dinitronaphthylamine, which crystallises in thin, dark yellow needles melting at about 218°. With acetic anhydride, it does not yield an acetyl derivative. This compound closely resembles the 1:6-dinitronaphthylamine of Gäss (Abstr., 1894, i, 605), but differs from it in melting point. When treated with nitrous acid, it yields nitronaphthalenediazoxide, which has also been obtained by Gäss. It follows from this that one of the nitro-groups is in position 1; the other is situated in the other ring, probably in position 6, since chlorodinitronaphthalene is converted by oxidation into a mononitrophthalic acid free from chlorine.

Aniline converts the chloro-compound into phenyldinitronaphthylamine, crystallising in slender, yellow needles, and α - and β -naphthylamine react in a similar manner.

2-Chloro-1:8-dinitronaphthalene can also be obtained by the nitration of β -chloronaphthalene under special conditions, and crystallises in thin, lustreless, yellow needles melting at 175°. With alcoholic ammonia, it yields 1:8-dinitro-2-naphthylamine, which crystallises in brown tablets melting at 222°, and can readily be converted, by means of the diazo-reaction, into 1:8-dinitronaphthalene. A chlorotrinitronaphthalene (probably 2-chloro-1:6:8-trinitronaphthalene) accompanies the dinitro-compounds and melts at about 145°.

A. H.

A Potassium Derivative of Fluorene. By RUDOLF WEISSGERBER (*Ber.*, 1901, **34**, 1659—1661).—In accord with the recently observed acid nature of the methylene group of fluorene, the latter, when fused with potassium hydroxide at 280°, yields a potassium derivative, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CHK}$, which forms a yellowish-brown, amorphous mass readily absorptive of water and carbon dioxide. The formation of this compound can be utilised to purify commercial fluorene, as it is readily decomposed by water, yielding the parent hydrocarbon. With compounds containing halogens, it readily combines; thus with benzyl chloride it yields phenyldiphenylene-ethane, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CH} \cdot \text{CH}_2\text{Ph}$, which crystallises from heavy petroleum in long, colourless prisms and melts at 149—150°. A small quantity of bis-diphenylene-ethane,



(De la Harpe and van Dorp, this Journal, 1876, i, 242; Graebe, Abstr., 1893, i, 38) is also formed.

Indene fails to yield a potassium compound, although the corresponding derivative of cyclopentadiene has recently been isolated (Thiele, this vol., i, 182).

W. A. D.

Fluorene. I. By OTTÒ DIELS (*Ber.*, 1901, **34**, 1758—1768).—2-Nitrofluorene (Strasburger, Abstr., 1884, 754) is best reduced to 2-aminofluorene by the action of zinc dust and calcium chloride on an

aqueous alcoholic solution; 2-aminofluorene crystallises in needles and melts at 130° (corr.). Strasburger (*loc. cit.*) gives the m. p. as $124\text{--}125^{\circ}$.

2-Diazofluorene chloride, $\text{CH}_2\text{--}\text{C}_6\text{H}_4\text{--}\text{C}_6\text{H}_3\text{--}\text{N}_2\text{Cl}$, forms minute, yellow needles containing $2\text{H}_2\text{O}$, decomposes at $119\text{--}120^{\circ}$ (corr.), dissolves in 40 parts of water at 18° , is more readily soluble in hot water, from which it crystallises on cooling, but is decomposed when boiled with water; the bromide forms white, felted needles, the iodide is yellow, the mercurichloride and platinichloride are yellowish, and the dichromate is orange-coloured.

2-Hydroxyfluorene, $\text{C}_{13}\text{H}_9\text{--OH}$, prepared by boiling the diazochloride with water, sinters at 166° and melts at 171° (corr.), is slightly soluble in hot water, from which it crystallises in flakes, dissolves readily in dilute alkalis and in organic solvents, and gives no coloration with ferric chloride; the potassium salt is precipitated in minute needles on adding concentrated potassium hydroxide to its aqueous solution.

2-Fluorylhydrazine, $\text{C}_{13}\text{H}_9\text{--N}_2\text{H}_3$, crystallises from hot alcohol in colourless flakes and from chloroform in four-sided, rhombic tablets, sinters at 165° , and melts at $170\text{--}171^{\circ}$ (corr.), reduces Fehling's solution and silver solutions; the chloride and sulphate crystallise in flakes and are only slightly soluble in water.

Benzylidenefluorylhydrazine, $\text{C}_{13}\text{H}_9\text{--NH--N--CHPh}$, crystallises from ethyl acetate in yellowish, glistening tablets, sinters at 182° , and melts at about 188° . Furfurylidenefluorylhydrazine, $\text{C}_{13}\text{H}_9\text{--NH--N--C}_5\text{H}_4\text{O}$, crystallises from ethyl acetate in glistening, brownish flakes, and melts at $190\text{--}191^{\circ}$ (corr.). β -Propylidenefluorylhydrazine, $\text{C}_{13}\text{H}_9\text{--NH--N--CMe}_2$, crystallises from hot alcohol in brownish tablets, sinters at 125° , and melts at $137\text{--}138^{\circ}$ (corr.). Ethyl acetoacetate fluorylhydrazone, $\text{C}_{19}\text{H}_{20}\text{O}_2\text{N}_2$, crystallises from alcohol in glistening, yellowish needles and melts at 124° (corr.).

2-Nitrofluorenone, $\text{CO--C}_6\text{H}_4\text{--C}_6\text{H}_3\text{--NO}_2$, previously obtained by nitrating diphenylene ketone, can also be prepared by oxidising nitrofluorene with acetic acid and potassium dichromate. 2-Aminofluorenone,

$\text{CO--C}_6\text{H}_4\text{--C}_6\text{H}_3\text{--NH}_2$, prepared by reducing the preceding compound with ammonia and hydrogen sulphide, crystallises from alcohol in deep violet-red, stout, glistening prisms, sinters at 156° , melts at 163° (corr.) to a deep-red liquid, is insoluble in water, but soluble in most organic solvents; the hydrochloride, $\text{C}_{13}\text{H}_9\text{ON}_3\text{--HCl}$, crystallises from acid solution in glistening, yellowish prisms, reddens a pine splinter, and is decomposed by water. The phenylhydrazone, $\text{C}_{19}\text{H}_{15}\text{N}_3$, forms golden-yellow crystals, sinters at about 138° and melts at about 148° (corr.).

4-Aminodiphenylcarboxylic acid, $\text{NH}_2\text{--C}_{12}\text{H}_8\text{--CO}_2\text{H}$, prepared by fusing aminofluorenone with potassium hydroxide, crystallises from hot water or alcohol in colourless needles and melts at about 215° .

2-Diazofluorenone chloride forms small, glistening, yellow needles, decomposes at 128° , and crystallises from hot water, but is decomposed by boiling. 2-Hydroxyfluorenone, $\text{C}_{13}\text{H}_8\text{O}_2$, crystallises from dilute acetic

acid in glistening, alizarin-red needles, sublimes below the melting point, sinters at 200° , melts at $210\text{--}211^{\circ}$ (corr.), dissolves in alkalis and less readily in ammonia. 2-Aminofluorene alcohol, $C_{13}H_{11}ON$, prepared by reducing an alcoholic solution of nitrofluorenone with zinc dust and calcium chloride, crystallises from hot alcohol in colourless, iridescent needles, sinters at 192° , and melts at 200° (corr.); the hydrochloride, nitrate, and sulphate crystallise in prisms. T. M. L.

Action of isoButylene Dibromide on Benzene in the presence of Aluminium Chloride. By F. BODROUX (*Compt. rend.*, 1901, 132, 1333—1336. Compare this vol., i, 196).—isoButylene dibromide, acting on benzene in the presence of aluminium chloride, gives rise to α -phenyl- β -methylpropane, $CH_2Ph \cdot CHMe_2$, $\alpha\beta$ -diphenyl- β -methylpropane, $CH_2Ph \cdot CMe_2Ph$, and a small amount of a substance crystallising from alcohol in colourless prisms and melting at 128° .

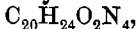
The first of these hydrocarbons is a colourless liquid having an agreeable odour and boiling at $171\text{--}173^{\circ}$ under a pressure of 750 mm.; its constitution is determined by treating it with excess of bromine and aluminium bromide when it gives rise to nonabromoisobutylbenzene, $C_6Br_5 \cdot C_4H_5Br_4$, melting at $216\text{--}217^{\circ}$, and a small amount of hexabromobenzene. Under these conditions, the isomeride, CMe_3Ph , yields only hexabromobenzene.

The second hydrocarbon is a pale yellow liquid having a blue fluorescence; it boils at $284\text{--}287^{\circ}$ under 750 mm. pressure, and has a sp. gr. 0.984 at 15° . When treated with excess of bromine and aluminium bromide, the compound undergoes fission at the quaternary carbon atom, and yields a mixture of nonabromoisobutylbenzene and hexabromobenzene. G. T. M.

Direct Production of Aromatic Amines from the Hydrocarbon. By CARL GRAEBE (*Ber.*, 1901, 34, 1778—1781).—Aniline is produced in small quantities by the action of hydroxylamine on benzene in presence of aluminium or ferric chloride, but not in presence of zinc chloride. Toluene gives a mixture of *p*-toluidine with a little *o*-toluidine, *o*-xylene gives a relatively good yield of 4-amino-1:2-xylene; *m*-xylene gives 4-amino-1:3-xylene, and *p*-xylene gives a small amount of 2-amino-1:4-xylene. Mesitylene is partially converted into mesidine. Naphthalene gives a small yield of α - and β -naphthylamines.

Phenylhydroxylamine, *p*-tolylhydroxylamine, and benzophenone-oxime undergo secondary changes when heated with benzene and aluminium chloride, and do not yield any appreciable quantity of condensation product. T. M. L.

Oxidising Action of Mercury Fulminate on Dimethylaniline. By ROLAND SCHOLL and E. BERTSCH (*Ber.*, 1901, 34, 2036—2039).—Tetramethyl-4:4'-diaminodiphenylmethane and a yellow base,



are produced when mercuric fulminate reacts with dimethylaniline at $160\text{--}170^{\circ}$. The yellow base is sparingly soluble in alcohol, and is best purified by solution in chloroform and precipitation with ether; it melts at 208° , and is readily soluble in chloroform or acetone.

The *hydrochloride*, $C_{20}H_{24}O_2N_4 \cdot 2HCl$, forms colourless crystals, the *picrate*, $C_{20}H_{24}O_2N_4 \cdot 2C_6H_3O_7N_4$, yellow needles melting at 192° , the *platinichloride*, yellowish-red needles, the *mercurichloride*,

$C_{20}H_{24}O_2N_4 \cdot 2HCl \cdot HgCl_2$, colourless needles. The base does not react with phenylhydrazine or hydroxylamine, but on treatment with nitrous acid yields a mixture of two isomeric *dinitro*-derivatives. The α -compound melts at 201 – 202° and is readily soluble in chloroform or acetone; the β -derivative forms yellow needles, melts at 225° , and is sparingly soluble in chloroform containing a little alcohol.
J. J. S.

Formation of Chains. LV. Derivatives of Phenoxyacetamide and -anilide. By CARL A. BISCHOFF [and, in part, with J. BLOCH, S. GERBERT, F. MITT, A. PESSIS, and S. WEBSCHOW] (*Ber.*, 1901, 34, 1835–1843).—The reactions between sodium phenoxide and α -bromo-derivatives of the fatty acid amides in indifferent solvents have been studied quantitatively. When heated until the products give a neutral reaction, more than 90 per cent. of the α -condensation product is obtained in each case. When warmed for 1 hour in benzene solution, the quantities obtained, calculated from the amount of sodium bromide formed, were with: α -bromopropionamide, 95–96; α -bromopropionanilide, 27–30; α -bromobutyramide, 92–95; α -bromobutyranilide, 16–19; α -bromoisobutyramide, 64; α -bromoisobutyranilide, 32–33; α -bromoisovaleramide, 37–39; α -bromoisovaleranilide, 16 per cent. α -Bromopropionamide distils at 135° under 19 mm. pressure, and the product obtained by the action of sodium phenoxide is identical with Saarbach's α -phenoxypropionamide (*Abstr.*, 1879, 642). α -Phenoxybutyramide melts at 123° , and not at 111° as stated by Luchmann (*Abstr.*, 1896, i, 544). α -Bromoisobutyramide distils at 145° under 17 mm. pressure; α -phenoxyisobutyramide crystallises in alcohol in stout needles melting at 114° . α -Phenoxyisovaleramide crystallises in felted needles melting at 143° . α -Phenoxyacetanilide obtained from sodium phenoxide and chloroacetanilide melts at 101.5° ; Morel (*Bull. Soc. Chim.*, 1899, [iii], 21, 964) gives 99 – 100° . α -Bromopropionylanilide distils at 186° under 19 mm. pressure, and α -phenoxypropionylanilide,

$OPh \cdot CHMe \cdot CO \cdot NHPh$, crystallises from light petroleum in rhombic plates melting at 118.5 – 119° , and distilling at 211 – 212° under 14 mm. pressure; it may also be prepared by the action of aniline on α -phenoxypropionylchloride, which distils at 146 – 147° under 55 mm. pressure. α -Phenoxybutyranilide, $OPh \cdot CHEt \cdot CO \cdot NHPh$, crystallises in colourless needles melting at 93 – 94° . α -Phenoxyisobutyranilide also melts at 93° and distils at 210 – 211° under 16 mm. pressure; when hydrolysed with alcoholic potash and a little water, it yields α -phenoxyisobutyric acid, the chloride of which cannot be distilled under reduced pressure without decomposition. α -Phenoxyisovaleranilide crystallises in branching needles melting at 97° .
J. J. S.

Formation of Chains. LVI. Toluidides and Naphthalides of Phenoxy-fatty Acids. By CARL A. BISCHOFF (*Ber.*, 1901, 34, 1844–1854. Compare preceding abstract).—The compounds described

have been obtained by the action of sodium phenoxide on the toluidides and naphthalides of brominated fatty acids.

[With L. KONKOROWITSCH.]—*α-Phenoxypropionyl-o-toluidide* crystallises from alcohol in colourless needles melting at 88—90°; *α-phenoxybutyryl-o-toluidide* melts at 101—102°. *α-Bromoisobutyryl-o-toluidide* cannot be distilled under reduced pressure without decomposition; on treatment with sodium phenoxide, it yields both *α-* and *β-phenoxyisobutyryl-o-toluidides*, melting respectively at 62° and 91°, but no toluidide of methacrylic acid. *α-Phenoxyisovaleryl-o-toluidide* crystallises in needles and melts at 116—117°.

[With N. GOLDBLATT.]—*α-Phenoxypropionyl-m-toluidide* crystallises in hexagonal plates melting at 86·5° and distilling at 220° under 15 mm. pressure. *α-Phenoxybutyryl-m-toluidide* forms prismatic needles melting at 92·5°, and the *isobutyryl* compound cruciform needles melting at 83°. *α-Phenoxyisovaleryl-m-toluidide* melts at 89—90°.

[With J. LIEBERMANN.]—*α-Phenoxypropionyl-p-toluidide* melts at 115°, the *butyryl* compound at 124°, the *isobutyryl* compound also at 124°, and the *isovaleryl* compound at 122°.

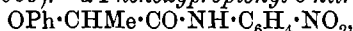
[With S. GERBERT.]—The percentage amounts of the substances which have reacted at the end of an hour are the same for the *m-* and *p-*propionyl and *isovaleryl* compounds. With *isobutyryl* compounds, the ortho-derivative more readily reacts, and with *butyryl* compounds, the meta-derivative less readily than the ortho and para.

[With P. MESCHLUMJANZ.] — *α-Phenoxypropionyl-α-naphthalide*, $\text{OPh}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, crystallises in small needles, melts at 131°, and distils at 260° under 20 mm. pressure; it is only sparingly soluble in ether or light petroleum. The *butyryl* compound melts at 148° and distils at 260° under 15 mm. pressure, the *isobutyryl* compound crystallises in prisms melting at 98°, and the *isovaleryl* compound in needles melting at 102°.

[With J. FEIGIN.]—*α-Phenoxypropionyl-β-naphthalide* melts at 117°, the *butyryl* compound also at 117°; the *isobutyryl* at 157·5°, and the *isovaleryl* at 128°.

In all cases, the *β*-derivatives are formed less readily than the isomeric *α*-compounds. J. J. S.

Formation of Chains. LVII. Nitroanilides of Phenoxy-fatty Acids. By CARL A. BISCHOFF [and, in part, with S. GERBERT, S. HIRSCHFELD, K. KRAUSE, F. MITT, and A. WATSCHJANZ] (*Ber.*, 1901, 34, 2057—2069).—*α-Phenoxypropionyl-o-nitroanilide*,



crystallises in yellowish, stout prisms or needles, melts at 88°, distils at 248° under 28 mm. pressure, and is readily soluble in most solvents. *α-Phenoxybutyryl-o-nitroanilide* was only obtained in the form of an impure oil. The *isobutyryl* compound crystallises from light petroleum in lemon-yellow needles, melts at 71°, distils at 236—237° under 17 mm. pressure, and is readily soluble. *α-Phenoxyisovaleryl-o-nitroanilide* was obtained in the form of an oil from which well-developed, flat plates melting at 47° separated. The following isomeric *m-* and *p-* compounds have also been prepared:

| | Meta. m.p. | Para. m.p. |
|-----------------|---------------|----------------------|
| Propionyl | 118° prisms. | 141—142° prisms. |
| Butyryl .. | 81° plates. | 108° minute needles. |
| isoButyryl..... | 119° needles. | 182° needles. |
| isoValeryl..... | 77° plates. | 125° needles. |

Most of the compounds have been prepared both by the action of sodium phenoxide on the nitroanilides of α -bromo-fatty acids, and also by the action of nitroanilines on the acid chlorides of phenoxy-fatty acids. The products obtained by the former method were often oily and did not admit of purification. By the reaction of sodium phenoxide on α -bromoisobutyryl-*p*-nitroanilide in benzene, a small amount of β -phenoxyisobutyryl-*p*-nitroanilide, $\text{OPh}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, was also obtained. It forms glistening, pale-yellow plates melting at 109°.

A tabulated statement is given of the yields obtained by heating together equivalent quantities of sodium phenoxide and the respective bromo-fatty nitroanilides for 1 hour in benzene. J. J. S.

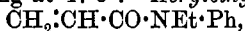
Formation of Chains. LVIII. Reaction of Sodium Phenoxide with Derivatives of α -Bromo-fatty Acids and Methyl- and Ethyl-aniline. By CARL A. BISCHOFF [and in part J. BLOCH, A. PESSIS, and S. WERSCHOW] (*Ber.*, 1901, 34, 2125—2135. Compare preceding abstract).—*Chloroacetylmethylanilide*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NMePh}$,

prepared from methylaniline and chloroacetyl chloride, crystallises in prismatic plates melting at 48°, the corresponding *bromo*-derivative forms prismatic plates melting at 69°. *Phenoxyacetylmethylanilide*, $\text{OPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NMePh}$, prepared by boiling mol. proportions of either of the foregoing substances and sodium phenoxide in solution in toluene, crystallises in right angled plates melting at 94°. *α -Phenoxypropionylmethylanilide*, $\text{OPh}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NMePh}$, prepared from α -bromopropionylmethylanilide and sodium phenoxide (yield 81 per cent.), crystallises in rhombic plates melting at 57.5° and boiling at 206° under 18 mm. pressure. By the action of sodium phenoxide on bromobutyrylmethylanilide, the expected phenoxyanilide was not obtained, but a mixture of phenol and crotonylmethylanilide. *α -Phenoxybutyryl chloride*, $\text{OPh}\cdot\text{CHEt}\cdot\text{COCl}$, prepared from the corresponding acid and phosphorus pentachloride, is a colourless oil boiling at 128—131° under 38 mm. pressure. *α -Phenoxybutyrylmethylanilide*, obtained from methylaniline and the last-mentioned compound, is a viscous oil boiling at 245—248° under 69 mm. pressure.

From α -bromoisobutyrylmethylanilide and sodium phenoxide is obtained a product which, on fractionation under pressure, is resolved into *α -methylacrylmethylanilide*, $\text{CH}_2\cdot\text{CMe}\cdot\text{CO}\cdot\text{NMePh}$, prismatic plates melting at 57° and boiling at 177° under 33 mm. pressure, and *α -phenoxyisobutyrylmethylanilide*, $\text{OPh}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NMePh}$, a colourless oil boiling at 210—211° under 24 mm. pressure. The latter substance could not be prepared from methylaniline and *α -phenoxyisobutyryl chloride*. *α -Bromoisovalerylmethylanilide* and sodium phenoxide yield,

together with a mixture of phenols, $\beta\beta$ -dimethylacrylmethylanilide, $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{NMePh}$, which forms a colourless oil boiling at $166\text{--}168^\circ$ under 36 mm. pressure.

α -Phenoxypropionylethylanilide, $\text{OPh}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NEtPh}$, prepared from α -bromopropionylethylaniline and sodium phenoxide, crystallises in rhombic prisms melting at $47\cdot5^\circ$. Acrylethylanilide,



is obtained as a by-product and forms an oil boiling at $150\text{--}160^\circ$ under 17 mm. pressure.

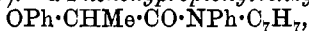
From α -bromobutyrylethylaniline and sodium phenoxide, crotonylethylanilide, $\text{CHMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{NEtPh}$, and a small quantity of α -phenoxybutyrylethylanilide are obtained. The former is an oil boiling at $167\text{--}168^\circ$ under 11—12 mm. pressure, the latter boils at about $210\text{--}220^\circ$ under the same pressure, but was not obtained in a pure state.

α -Methylacrylethylanilide, $\text{CH}_2\cdot\text{CMe}\cdot\text{CO}\cdot\text{NEtPh}$, is the only product of the interaction of α -bromoisobutyrylethylanilide and sodium phenoxide, and forms an oil boiling at 161° under 20 mm. pressure. $\beta\beta$ -Dimethylacrylethylanilide, $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{NEtPh}$, obtained by the action of sodium phenoxide on α -bromoisovalerylethylanilide, boils at 165° under 18 mm. pressure.

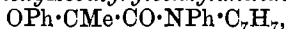
It is seen that an increase in length of the carbon chain of the acyl group decreases the amount of phenoxy-derivatives and promotes the formation of derivatives of acrylic acid.

K. J. P. O.

Formation of Chains. LIX. Reaction of Sodium Phenoxide with Derivatives of α -Bromo-fatty Acids and Benzaniline, Diphenylamine, and Carbazole. By CARL A. BISCHOFF [and in part P. DENISSENKO, S. GERBERT, W. KISSIN, and F. MITT] (*Ber.*, 1901, 34, 2135—2145).— α -Phenoxypropionylbenzylanilide,



prepared from α -bromopropionylbenzylanilide and sodium phenoxide, crystallises in lustrous prisms melting at $111\text{--}112^\circ$. α -Bromobutyrylbenzylanilide and sodium phenoxide yield mainly crotonylbenzylanilide, $\text{CHMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{NPh}\cdot\text{C}_7\text{H}_7$, forming colourless crystals melting at 82° , and a small quantity of α -phenoxybutyrylbenzylanilide, which was also obtained by the action of α -phenoxybutyryl chloride on benzylaniline, and crystallises in needles melting at 65° and boiling at 245° under 15 mm. pressure. α -Phenoxyisobutyrylbenzylanilide,



could only be prepared from the acid chloride and the base, and crystallises in large, prismatic plates melting at $52\text{--}53^\circ$. By the action of sodium phenoxide on α -bromoisobutyrylbenzylanilide only methylacrylbenzylanilide is obtained. The latter substance forms an oil boiling at 204° under 15 mm. pressure. α -Phenoxyisovalerylbenzylanilide, $\text{OPh}\cdot\text{CHPr}^s\cdot\text{CO}\cdot\text{NPh}\cdot\text{C}_7\text{H}_7$, is similarly only procurable from the acid chloride and the base, and crystallises in right angled plates melting at 67° . From α -bromoisovalerylbenzylanilide and sodium phenoxide, $\beta\beta$ -dimethylacrylbenzylanilide is formed as a yellowish oil boiling at 226° under 20 mm. pressure. α -Phenoxypropionyl diphenylamide, $\text{OPh}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NPh}_2$, prepared by the action of sodium phenoxide on

α -bromopropionyldiphenylamide, crystallises in long, colourless prisms melting at 93° . The corresponding butyryl compound could not be obtained from α -bromobutyrylphenylamide; *crotonyldiphenylamide*, $\text{CHMe}:\text{CH}\cdot\text{CO}\cdot\text{NPh}_2$, was the only product, and formed small prisms melting at 115 – 116° . *α -Phenoxybutyryldiphenylamide*, prepared from diphenylamine and α -phenoxybutyryl chloride, crystallises in colourless leaflets melting at 67° . α -Bromo*isobutyryldiphenylamide* and sodium phenoxide yield only *α -methylacryldiphenylamide*, which crystallises in right angled plates or needles melting at 108° . The phenoxy-compound was not formed, neither could it be prepared from α -phenoxy*isobutyryl chloride* and diphenylamine. Similarly, $\beta\beta$ -*dimethylacryldiphenylamide*, $\text{CMe}_2:\text{CH}\cdot\text{CO}\cdot\text{NPh}_2$, is alone produced from sodium phenoxide and α -bromo*isovaleryldiphenylamide* and forms needles melting at 99° .

α -Bromo-, propionyl, butyryl, and *isovaleryl* derivatives of carbazole only react with sodium phenoxide when heated in boiling nitrobenzene. In all cases, sodium bromide and carbazole were the only products isolated.

The results in this and previous papers are discussed.

K. J. P. O.

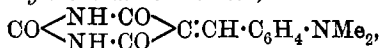
Reduction of Phenylthiocarbimide. By ALEXANDER GUTBIER (*Ber.*, 1901, 34, 2033–2034).—When reduced in acid solution, thiocarbimides yield primary amines and thioformaldehyde, but phenylthiocarbimide, when reduced with aluminium amalgam in neutral solution, yields *s*-diphenylthiocarbamide and methyl mercaptan, the latter being probably formed by the reduction of thioformaldehyde which is first produced.

J. J. S.

Condensation of Barbituric Acid with Aromatic Aldehydes to Coloured Substances. By ARTHUR WEINSCHENK (*Ber.*, 1901, 34, 1685–1687).—Barbituric acid, which with ortho-substituted benzaldehydes (Conrad and Reinbach, this vol., i, 410) yields colourless substances, with para-substituted derivatives yields coloured products.

p-Hydroxybenzylidenobarbituric acid, $\text{CO} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} \text{C}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, prepared by using *p*-hydroxybenzaldehyde, crystallises from alcohol in canary-yellow, microscopic prisms, and does not melt at 300° ; with dilute potassium hydroxide, it yields a reddish-yellow potassium salt, but is readily resolved into its components by an excess of the alkali.

p-Dimethylaminobenzylidenobarbituric acid,



obtained from *p*-dimethylaminobenzaldehyde, is an orange-red, crystalline powder which sinters at 270° and melts and decomposes at 282° ; the hydrochloride forms stellate aggregates of orange coloured needles.

W. A. D.

Action of *p*-Xylylene Bromide on some Primary, Secondary, and Tertiary Amines and Alkaloids. By WAHAN MANOUKIAN (*Ber.*, 1901, 34, 2082–2092).—*p*-Xylylene bromide differs in some respects

from *o*-xylylene bromide (Scholtz, Abstr., 1898, i, 305) in its action on amines. It does not yield ring compounds of the type of dihydro-isoindole with primary amines, and does not form ammonium bromides with secondary amines.

p-Xylylenedi- α -naphthylamine, $C_6H_4(CH_2 \cdot NH \cdot C_{10}H_7)_2$, obtained by the action of *p*-xylylene bromide on α -naphthylamine in chloroform solution, is a white, crystalline powder melting at 165° . *p*-Xylylenediisobutylamine crystallises in large prisms melting at 65° ; the *platinichloride* crystallises in large red prisms melting at 220° ; the *aurichloride* forms slender needles melting at 205° ; and the *picrate* melts at 171° . *p*-Xylylenedidiphenylamine, $C_6H_4(CH_2 \cdot NPh_2)_2$, crystallises in small, light green needles melting at 186° . *p*-Xylylenedipiperidine crystallises in transparent leaflets melting at 86° ; the *platinichloride* decomposes at about 250° ; the *aurichloride* crystallises in large, yellow needles melting at 215° , and the *picrate* melts at 221° . *p*-Xylyleneditriethylammonium bromide, $C_6H_4(CH_2 \cdot NEt_3Br)_2$, is formed by the direct combination of *p*-xylylene bromide with triethylamine, and crystallises in large, colourless needles melting at 230° ; the *perbromide*, $C_6H_4(CH_2 \cdot NEt_3Br_3)_2$, is an orange-yellow precipitate which melts at 164° ; the *platinichloride* crystallises in orange coloured prisms melting at 238° , and the *aurichloride* crystallises in yellow needles melting at 242° . *p*-Xylyleneditripropylammonium bromide forms small needles melting at 223° ; the *perbromide* melts at 181 – 182° ; the *platinichloride* melts at 235° , and the *aurichloride* at 214° . *p*-Xylylenedipyridinium bromide crystallises in small needles melting at 260° ; the *perbromide* melts at 149° , the *platinichloride* at 253° , and the *aurichloride* at 246° . *p*-Xylylenediquinolinium bromide crystallises in pale violet, microscopic needles melting at 306° ; the *perbromide* melts at 206° , the *platinichloride* at 257° , and the *aurichloride* at 242° . With strychnine, *p*-xylylene bromide yields *p*-xylylenedistrychninium bromide, which crystallises in microscopic needles melting at 291° ; the *perbromide* melts at 195° , the *platinichloride* at 247 – 249° , and the *aurichloride* at 210° . Morphine and quinine, on the other hand, yield mixtures of the monoammonium and diammonium compounds, which cannot easily be separated into their constituents.

A. H.

Action of Methyl on the Velocity of Reaction of the β -Aromatic Hydroxylamines. By EUGEN BAMBERGER and ADOLF RISING (*Annalen*, 1901, 316, 257–292. Compare Abstr., 1898, i, 20).—The formation of an azoxy-derivative by the interaction of a β -aromatic hydroxylamine with the corresponding nitroso-compound has been employed in studying the influence of the orientation of substituent methyl radicles on the velocity of reaction. The reagents were mixed in alcoholic solutions maintained at 15.2 – 15.3° , and from time to time samples were taken and tested with Fehling's solution, the amount of reduction being a measure of the quantity of unaltered hydroxylamine derivative. The compounds containing no methyl groups, or having these substituents in meta-positions, react most rapidly, the para-substituted derivatives are much less active, and the ortho-substituted derivatives are affected least of

all. The three tolylhydroxylamines and the corresponding nitroso-compounds were employed in demonstrating this generalisation. The rule applies also to the xylene compounds, 1:3-xylyl-2-hydroxylamine being the least active of any of these derivatives.

2-Azoxy-1:3-xylene is obtained in small yield when 1:3-xylyl-2-hydroxylamine is boiled for 12 hours with an alcoholic solution of 2-nitroso-1:3-xylene; it crystallises in straw-yellow needles melting at 88.5—89° and is readily soluble in the ordinary organic solvents. Mesitylhydroxylamine and nitrosomesitylene, which contain methyl groups both in the para- and in the two ortho-positions, do not exhibit any tendency to undergo condensation.

1:2-Xylene-4-hydroxylamine, prepared by reducing 4-nitro-1:2-xylene with zinc dust in the presence of a dilute alcoholic solution of ammonium chloride, crystallises from benzene in white needles melting at 98—101°. It readily dissolves in ether, alcohol, acetone, or light petroleum, and its solution in these solvents, when maintained for several hours at the boiling point, yields a mixture of 4-amino-1:3-xylene and the corresponding azoxyxylene. 4-Nitroso-1:3-xylene, obtained either as an intermediate product in the preceding experiments or by oxidising 1:2-xylene-4-hydroxylamine with a cold solution of ferric chloride, crystallises from alcohol in light bluish-green needles melting at 44—45°; when dried for 12 days on porous plates, the green crystals become yellow; the melting point, however, remains unaltered, and the green colour is recovered on distilling the product in steam.

4-Azoxy-1:2-xylene crystallises from light petroleum in light canary-yellow needles and melts at 140—140.5°.

1:2-Xylyl-3-hydroxylamine crystallises in snow-white leaflets and melts at 74°, the yield of the base from the corresponding nitro-compound being 55—60 per cent.

3-Nitroso-1:2-xylene crystallises in white needles and melts at 91—91.5°, at the same time becoming green in colour; the corresponding azoxy-compound is obtained in lustrous, almost colourless needles and melts at 116.5°.

1:4-Xylyl-3-hydroxylamine crystallises in white needles and melts at 91.5°; it is soluble in the ordinary organic solvents, with the exception of light petroleum; the corresponding nitroso-compound crystallises in white, silky needles melting at 101.5°; the azoxy-compound is prepared either by the interaction of the two preceding compounds, or from the hydroxylamine, either by atmospheric oxidation in aqueous solution, or by heating the base on the water-bath, in the latter case being accompanied by *p*-xylidine; when absolutely pure, it is colourless, but in general forms pale yellow, lustrous needles melting at 110—110.5°.

On digesting the aromatic hydroxylamines with dilute sulphuric acid (1:15) at 15°, those containing methyl groups in the ortho-position with respect to the nitrogen atom are most readily decomposed; phenylhydroxylamine and 1:3-xylyl-2-hydroxylamine require for their complete decomposition 8 days and 6 minutes respectively, whilst mesitylhydroxylamine is destroyed instantaneously. The paper also contains details of the preparation of the tolylhydroxylamines and

the corresponding nitroso-compounds; *o*-tolylhydroxylamine, formerly described as an oil (Abstr., 1895, i, 217), is found to melt at 44°.

The orientation of the substituent methyl groups exerts a very marked influence on the interaction of the aromatic hydroxylamines with benzenediazonium chloride. The reaction was in each case carried out in alcoholic solution at 0°, the time allowed for the experiment being 80 minutes. Under these conditions, a yield of 98·5 per cent. of benzeneazohydroxyanilide is obtained from phenylhydroxylamine; *m*-tolylhydroxylamine yields 96·6 per cent. of benzeneazohydroxy-*m*-toluidide, which melts at 125·5°. Benzeneazohydroxy-*p*-toluidide, melting at 124°, is obtained in a similar manner from *p*-tolylhydroxylamine, the yield being 90·3 per cent.; in the case of benzeneazohydroxy-*o*-toluidide (Abstr., 1899, i, 687), the yield is 75 per cent. 4-Benzeneazohydroxy-1:2-xylidide melts at 140—141°, the yield is 95·5 per cent.; 2-benzeneazohydroxy-1:4-xylidide, 3-benzeneazohydroxy-1:2-xylidide, 4-benzeneazohydroxy-1:3-xylidide, and 2-benzeneazohydroxy-1:3-xylidide melt at 111·5°, 105°, 82·5—83°, and 113° respectively, the yields of these compounds obtained by the general method being 79·2, 76·7, 51·9, and 31·1 per cent. respectively. All these azohydroxyamides crystallise in yellow needles, and yield characteristic insoluble, brownish-yellow copper derivatives. It will be seen that 2-benzeneazohydroxy-1:3-xylidide, which contains 2 methyl groups in the ortho-position with respect to the nitrogen atom, reacts least readily with the diazonium salt; when the para-position is also substituted, as in mesitylhydroxylamine, there is no interaction whatever, the latter base merely becoming oxidised, and yielding a small amount of nitroso-mesitylene.

G. T. M.

1:3-Xylyl-2-hydroxylamine and 2-Nitroso-1:3-xylene. By EUGEN BAMBERGER, and ADOLF RISING (*Annalen*, 1901, 316, 292—311. Compare preceding abstract).—1:3-Xylene-2-hydroxylamine (compare von Pechmann, Abstr., 1898, i, 310), prepared by reducing 2-nitro-1:3-xylene in alcoholic solution with zinc dust in the presence of ammonium chloride, crystallises in white, lustrous needles, and melts at 97—98·5°; it readily dissolves in the ordinary solvents, with the exception of light petroleum. The preceding base, when suspended in water and oxidised by a current of air, yields 2-amino-4-hydroxy-1:3-xylene, a substance crystallising from water or chloroform in lustrous needles melting at 180·5—181·5°, together with 2-nitroso-1:3-xylene (m. p. 141·5°), 1:3-xyloquinone, 1:3-xylidine, and a compound crystallising in white prisms and melting at 189°. 2-Amino-4-hydroxy-1:3-xylene, when dissolved in aqueous sodium hydroxide, yields at first a colourless solution, which becomes violet on exposure to air and on boiling evolves ammonia; when shaken with an alkaline solution of α -naphthol, a transient indophenol coloration is observed; the aminophenol yields, with salicylaldehyde, a copious, yellow precipitate, but does not give any colour reaction with ferric chloride. The sulphate, $C_8H_9NO_2 \cdot \frac{1}{2}H_2SO_4$, crystallises in white, lustrous needles and melts at 268°; when its solution is boiled, hydrolysis takes place, resulting in the formation of 2:5-dihydroxy-1:3-xylene.

2-Nitroso-1:3-xylene and nitrosomesitylene differ from their lower homologues in not possessing the characteristic irritating odour of nitrosobenzene; the colours of their solutions vary perceptibly with the temperature; this phenomenon is probably due to changes in the state of aggregation of the dissolved molecules. The cryoscopic molecular weight determination in benzene points to the existence of double molecules, and the ebullioscopic method indicates a certain degree of association, even in boiling acetone.

1:3-Xylyl-2-hydroxylamine, when treated with cold dilute sulphuric acid yields, in addition to the substances obtained by its atmospheric oxidation, 2-amino-5-hydroxy-1:3-xylene-4-sulphonic acid, and 2:2'-diamino-1:3-xylyl 5-oxide. The former of these products crystallises from water in lustrous, white needles, which, on treatment with alkaline α -naphthol solution, give an indophenol reaction; when boiled with a solution of sodium acetate, the sodium salt is produced, the reaction being a reversible one. The sulphonic acid, when heated with dilute hydrochloric acid at 160°, loses its sulphonic group, and becomes converted into 2-amino-5-hydroxy-1:3-xylene; at the same time, a portion of the latter compound undergoes further hydrolysis, resulting in the elimination of ammonia and the formation of 2:5-dihydroxy-1:3-xylene.

2:2'-Diamino-1:3-xylyl 5-oxide forms colourless, highly refractive needles or plates melting at 156·7—157°; its *hydrochloride* crystallises in leaflets melting at 320°, and furnishes a characteristic colour reaction with ferric chloride, the colour changing from violet to yellow, a red precipitate being formed at an intermediate stage; the mixture, on boiling, evolves 1:3-xyloquinone. The base, when diazotised, yields red azo-compounds with the naphthols; its *acetyl* derivative, obtained by the action of acetic anhydride on the water-bath, crystallises from alcohol in white, silky needles and melts at 283°.

1:3-Xylyl-2-hydroxylamine is very stable towards sodium hydroxide solution in the absence of air, and after 14 days only 4 per cent. of the base is converted into the corresponding nitroso-xylene; in the presence of oxygen, the oxidation follows the products previously indicated.
G. T. M.

Acidimetric Value (Avidity) of *p*-Sulphanilic Acid. By GUSTAVE MASSOL (*Compt. rend.*, 1901, 132, 1572—1573).—The heats of dissolution and neutralisation of anhydrous *p*-sulphanilic acid are -3·84 and 9·07 Cal. respectively, and the heats of dissolution of the dihydrated and anhydrous sodium salt are -7·84 and -1·64 Cal. respectively, the heat of hydration of the anhydrous compound being 3·34 Cal., and its heat of formation 18·08 Cal.

The heats of neutralisation of sulphurous, phenylsulphonic and *p*-sulphanilic acids are compared with those of carbonic, benzoic, and *p*-aminobenzoic acids, the diminution in avidity (measured in heat units), due to the introduction of amidogen, is 4·53 Cal. in the former case, and 1·37 Cal. in the latter.

In solution, *p*-aminobenzoic acid has a greater avidity than *p*-sulphanilic acid, the values being 12·12 and 9·07 Cal. respectively; in the

solid state, however, the latter acid is stronger, the corresponding values for the heats of neutralisation being 16.18 and 18.08 Cal.

G. T. M.

Hydrolysis of Phenol Ethers by Alcoholic Potash. By RICHARD STOERMER and BRUNO KAHLERT (*Ber.*, 1901, 34, 1812).—The authors find, in contradiction to the statement of Bouveault (*Abstr.*, 1899, i, 437), that the ethers of monoatomic phenols are hydrolysed by alcoholic potash, provided that the temperature be high and the time of action long. Anisole and phenetole both yield phenol when treated in this way for 15 hours at 180–200°. Anethole in the same way yields anol. A. H.

Action of Phenols on Ethylic Oxalate. By J. BISHOP TINGLE and LEO O'BYRNE (*Amer. Chem. J.*, 1901, 25, 496–501).—By the action of ethyl oxalate on thymol in presence of sodium, J. B. and A. Tingle (*Amer. Chem. J.*, 1899, 21, 261) obtained an oily condensation product which gives a dark red coloration with ferric chloride. The behaviour of the following substances under similar circumstances has been investigated: catechol, carvacrol, picric acid, β -naphthol, ethyl salicylate, quinone, guaiacol, resorcinol, phloroglucinol, quinol, anisole, and carvol. The first six of these showed no evidence of having reacted, whilst guaiacol yielded only tarry products. Resorcinol furnished a yellow, crystalline substance, which melts and decomposes at 257–258°, and is perhaps identical with the compound obtained by Michael (*Abstr.*, 1887, 949) by the interaction of resorcinol, ethyl oxalate, and sodium ethoxide. Phloroglucinol yielded a crystalline compound which softens at 305°, together with another substance which crystallises in plates and blackens without melting at 240°. With quinol, a substance was produced which blackens above 200° and remains unmelted at 300°. Anisole and carvol form oily condensation products, similar to that obtained from thymol, which give a deep red coloration with ferric chloride and alcohol; the substance prepared from carvol furnishes barium and copper salts, which, like the parent substance, readily become resinous; the resin has a strong odour of violets. E. G.

Ethers of *p*-Aminophenol and their Carbamide Derivatives. By LEOPOLD SPIEGEL and S. SABBATH (*Ber.*, 1901, 34, 1935–1947).—The ethers of *p*-aminophenol are all very poisonous and of no therapeutic value (differing from the acetyl derivative of the ethyl ether, "phenacetin"), also the carbamide derivatives have no sweet taste like *p*-phenetole- and *p*-anisole-carbamides ("dulcin").

The ethers of *p*-aminophenol are easily obtained by the reduction with tin and hydrochloric acid of the corresponding nitro-compounds, which are prepared by the action of halogen alkyls on potassium *p*-nitrophenoxide. The carbamide derivatives are best prepared by warming on a water-bath aqueous solutions of carbamide and the hydrochlorides of the amino-ethers, the thiocarbamides being obtained in a similar manner from ammonium thiocyanate. At higher temperatures, disubstituted carbamides are obtained; these, being insoluble in

water, are easily separated from the mono-derivatives, which are soluble in hot water.

p-Nitrophenyl propyl ether is a reddish oil which boils at 285—287° with slight decomposition; *p-aminophenyl propyl ether* is a very unstable, colourless oil, and forms a *hydrochloride* crystallising in needles and melting at 171°, a *platinichloride*, and a *picrate* which blackens at 162° and melts at 176°. *p-Propyloxyphenylcarbamide* crystallises in colourless leaflets melting at 147°, *di-p-propyloxyphenylcarbamide* in silky needles melting at 201°, and *p-propyloxyphenylthiocarbamide* in needles melting at 158°.

p-Nitrophenyl allyl ether is obtained in needles and melts at 36°; the corresponding *amino-compound* is a reddish-yellow oil which forms a colourless *hydrochloride* melting at 205°, a *platinichloride*, and a *picrate* crystallising in small, yellow needles which melt at 164°. *p-Allyloxyphenylcarbamide* crystallises in small needles and melts at 154°; *di-p-allyloxyphenylcarbamide* melts at 211°. *p-Allyloxyphenylthiocarbamide* crystallises in small needles and melts at 148°; the corresponding disubstituted *carbamide* is similar and melts at 161°. *p-Nitrophenyl amyl ether* is a reddish oil which boils at 309—310° with partial decomposition; *p-aminophenyl amyl ether* is a yellowish oil, and forms a *hydrochloride* melting at 236°, a microcrystalline *platinichloride*, and an *acetyl* derivative which crystallises in small, lustrous needles and melts at 97°; the monosubstituted *carbamide* melts at 133°, the disubstituted *carbamide* crystallises in silky needles melting at 170°, and the monosubstituted *thiocarbamide* crystallises in colourless leaflets and melts at 157°.

p-Nitrophenyl benzyl ether forms microscopic needles, melts at 108°, and, when reduced with iron filings and acetic acid, yields the corresponding *amino-compound*, which crystallises in colourless leaflets, melts at 56°, and forms a crystalline *hydrochloride* melting at 213°, a *platinichloride*, and a *picrate* melting and decomposing at 155°; *p-benzyl-oxyphenylcarbamide* crystallises in needles and melts at 174°.

p-Aminophenyl isobutyl ether is a colourless oil and forms a *hydrochloride* crystallising in long needles which melt at 209°, and a *picrate* melting at 155°; *p-isobutyloxyphenylcarbamide* crystallises in colourless prisms melting at 156°, and the corresponding *thiocarbamide* melts at 158°.

R. H. P.

Derivatives of Hydroxyquinol Triethyl Ether [1:2:4-Triethoxybenzene]. By E. BREZINA (*Monatsh.*, 1901, 22, 346—356. Compare Abstr., 1889, 247).—1:2:4-Triethoxybenzene is prepared from triacetoxybenzene by heating with ethyl iodide and potassium hydroxide. The mononitro-derivative ($\text{NO}_2=5$) is very readily formed, even by the action of dilute nitric acid on the ether, and is best prepared by nitrating in acetic acid solution; it crystallises in yellow needles melting at 108—109°. On reduction of the nitro-compound, an amino-derivative is obtained, which is oxidised by ferric chloride to 2:5-diethoxyquinone. 5-Bromo-1:2:4-triethoxybenzene, $\text{C}_6\text{H}_2\text{Br}(\text{OEt})_3$, prepared by brominating the ether, forms white crystals melting at 51—52°, and by nitric acid is converted into the nitro-derivative previously described. 3:5:6-Tribromo-1:2:4-

triethoxybenzene, prepared by the action of excess of bromine on the monobromo-compound at 100° , forms crystals melting at $72-73^{\circ}$. This substance is also obtained by the action of bromine on the mononitro-derivative at 100° , the nitro-group being replaced by bromine. Nitric acid does not replace bromine from the tribromo-compound.

K. J. P. O.

Diphenylene Oxide in Coal Tar and the derived Diphenol. By GUSTAV KRAEMER and RUDOLF WEISSGERBER (*Ber.*, 1901, 34, 1662—1667).—When the fluorene fraction of coal tar is purified by fusion with potassium hydroxide (this vol., i, 521), the aqueous alkaline solution contains a considerable quantity of 2:2'-dihydroxydiphenyl, which separates as a rapidly solidifying oil, and can be purified by recrystallisation from toluene. Contrary to the statement of Hodgkinson and Matthews (*Trans.*, 1882, 41, 168), the diphenol is not formed by repeatedly fusing pure fluorene with potassium hydroxide; its formation indicates the presence in commercial fluorene of diphenylene oxide, since the latter is converted into the diphenol on fusion with alkali. The yield of 2:2'-dihydroxydiphenyl from the oxide is considerably increased by carrying out the fusion in presence of phenanthrene as solvent. The converse transformation of the diphenol into the oxide is readily effected by fusion with zinc chloride.

The *sulphonic acid* derived from diphenylene oxide forms beautiful crystals, and is not hydrolysed by passing steam through its solution in sulphuric acid, although resolved on heating with hydrochloric acid under pressure. Diphenylene oxide differs from coumarone and furan in yielding a colourless solution in concentrated sulphuric acid.

2:2'-Dihydroxydiphenyl crystallises from water in lustrous leaflets which contain the solvent, melt at $73-75^{\circ}$, and effloresce in a desiccator; it boils at 315° under 768 mm. pressure. The *diacetyl* derivative separates from xylene in large, transparent crystals, and melts at 95° .

W. A. D.

Production of *o*-Hydroxyphenylethyl Alcohol from Coumarone and Synthesis of Hydrocoumarone. By RICHARD STOERMER and BRUNO KAHLERT (*Ber.*, 1901, 34, 1806—1811).—When coumarone is heated with alcoholic potash at 200° , decomposition occurs, and the product contains (1) a small amount of substance which can be extracted by ether from the alkaline solution, and probably contains an unsaturated hydrocarbon; (2) *o*-hydroxyphenylacetic acid melting at 145° ; and (3) a portion insoluble in sodium hydrogen carbonate. The last portion contains *o*-hydroxyphenylethyl alcohol,



which is a thick, almost colourless oil without characteristic smell, boils at $168-169^{\circ}$ under 12 mm. pressure, and has the sp. gr. 1.1531 at 18° , and the molecular refraction 38.5. The *sodium* salt is only sparingly soluble in aqueous soda. This compound and *o*-hydroxyphenylacetic acid are probably formed in the first instance by the simultaneous oxidation and reduction of hydroxyphenylacetaldehyde, produced by the splitting of the furfuran group of coumarone.

o-Hydroxyphenylethyl alcohol forms two compounds with phenyl-

cyanate; the *monourethane*, $C_{15}H_{15}O_3N$, crystallises in white plates melting at $116-117^\circ$; the *diurethane*,

$NHPh \cdot CO \cdot O \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot O \cdot CO \cdot NHPh$,
crystallises in white needles melting at 130° .

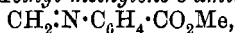
o-Hydroxyphenylethyl alcohol is converted by hydrogen bromide into the *bromide*, $OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2Br$, an unstable oil which on treatment with aqueous soda yields hydrocoumaroné, $C_6H_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} CH_2$.

o-Ethoxyphenylethyl alcohol boils at $136-137^\circ$ under 14 mm. pressure, and is converted by oxidation into *o*-ethoxybenzoic acid. The urethane, $OEt \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot O \cdot CO \cdot NHPh$, melts at 66° . A. H.

Action of Benzoyl Chloride on Ethyl Ether. By EDGAR WEDEKIND and J. HAEUSSERMANN (*Ber.*, 1901, 34, 2081—2082).—Acid chlorides react with ether in the presence of anhydrous ferric chloride, ethyl chloride and the ethyl ester of the corresponding acid being produced. In most cases, the extent of the reaction is small, but in the case of benzoyl chloride as much as half of the chloride is converted into ethyl benzoate. A similar action of acetyl chloride in presence of zinc chloride has been observed by Descudé (this vol., i, 357). A. H.

Preparation of Simple and Compound Anhydrides. By A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 404—410).—One of the most convenient methods of preparing benzoic anhydride is by the addition of benzoyl chloride (1 mol.) to a solution of benzoic acid (1 mol.) in pyridine (1 mol.). When the reaction is finished, the product, after washing successively with warm water, dilute hydrochloric acid, sodium hydroxide solution, and warm water, and drying by means of fused sodium sulphate, is pure benzoic anhydride; pyridine hydrochloride is also formed in the reaction. Acetic anhydride is similarly obtained by the interaction of acetyl chloride, acetic acid, and pyridine. Also by the action of benzoyl chloride on a pyridine solution of acetic acid, the mixed acetic benzoic anhydride is formed; this compound readily undergoes decomposition, partly even in the cold, yielding acetic and benzoic anhydrides. T. H. P.

Conversion of Derivatives of Anthranilic Acid into Indigo. By HUGO ERDMANN (*J. pr. Chem.*, 1901, [ii], 63, 385—391).—*Ethyl o*-aminobenzoylformate, $NH_2 \cdot C_6H_4 \cdot CO \cdot CO_2Et$, prepared by condensing ethyl formate and methyl *o*-aminobenzoate in the presence of sodium, forms colourless needles melting at 49° , which, on hydrolysis, yield only anthranilic acid. *Methyl methylene-o*-aminobenzoate,



obtained by the action of commercial formaldehyde on methyl *o*-aminobenzoate, crystallises in large, colourless crystals melting at 116.5° . With hydrogen bromide, it forms an unstable, yellow, additive product which melts and decomposes at 200° , and with bromine, a crystalline dibromide which, on heating at 175° , evolves carbon dioxide and yields a violet dye soluble in acids.

It is found that of all the derivatives of anthranilic acid, methyl *o*-cyanomethylacetaminobenzoate (see following abstract) yields indigo

most easily, and in quantity. The ester is heated with naphthalene at 150—170°, and potassium hydroxide added; from the product pure indigotin can be extracted, representing 48 per cent. of the original ester.

K. J. P. O.

Action of Formaldehyde and Nascent Hydrogen Cyanide on Anthranilic Acid. By EMIL KOHNER (*J. pr. Chem.*, 1901, [ii], 63, 392—404. Compare preceding abstract).—*Anthranilidoacetoneitrile* (*o*-cyanomethylaminobenzoic acid), $\text{CN}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, prepared by the gradual addition of powdered potassium cyanide and formaldehyde to a solution of anthranilic acid in acetic acid, crystallises from alcohol in yellowish scales, melting and decomposing at 181°. The yield of pure nitrile amounts to 84 per cent. of the anthranilic acid employed. The solutions exhibit a violet fluorescence. The sodium salt, $\text{C}_9\text{H}_7\text{O}_2\text{N}_2\text{Na}\cdot 5\text{H}_2\text{O}$, forms yellowish prisms, the silver and copper salts anhydrous powders. Hydrolysis with potassium hydroxide converts the acid into phenylglycine-*o*-carboxylic acid. The ethyl ester, prepared by the action of ethyl iodide on the silver salt, forms colourless crystals melting at 89°. The methyl ester is readily obtained by the addition of a solution of methyl sulphate in methyl alcohol to a well stirred aqueous solution of the sodium salt at 40—50°, an alkaline reaction being maintained during the process by addition of aqueous sodium carbonate; the compound crystallises in yellowish needles melting at 106.5°. Although the acid cannot be acetylated, the methyl ester readily yields an acetyl derivative, $\text{C}_{12}\text{H}_{12}\text{O}_3\text{N}_2$, which forms crystals melting at 82—83°.

The nitroso-derivative, $\text{C}_9\text{H}_7\text{O}_3\text{N}_3$, of *o*-cyanomethylaminobenzoic acid, forms a yellowish powder melting at 113—114°; the bromo-derivative, $\text{C}_9\text{H}_7\text{O}_2\text{N}_2\text{Br}$, crystallises in colourless plates melting at 210—212°. The bromo-derivative of the methyl ester, $\text{C}_{10}\text{H}_9\text{O}_2\text{N}_2\text{Br}$, forms colourless crystals melting at 141—142°.

K. J. P. O.

Condensation Products of Ethyl Cyanoacetate with Aldehydes. By CORRADO BERTINI (*Gazzetta*, 1901, 31, i, 265—279).—Compounds of the structure $\text{CHR}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, which are obtained by the condensation of aldehydes with ethyl cyanoacetate in presence of sodium ethoxide, should be capable of existing in two stereoisomeric modifications. By using piperidine as a condensing agent, the author finds that in some cases it is possible to obtain stereoisomerides of previously known compounds of this type.

The ethyl α -cyanocinnamate obtained from benzaldehyde and ethyl cyanoacetate in presence of sodium ethoxide is solid and melts at 51°. When piperidine is employed in place of the sodium ethoxide, however, a liquid ethyl α -cyanocinnamate, $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}$, is produced; it forms a faintly yellow oil insoluble in water and having a slight odour of bitter almonds; it is unchanged by long boiling in alcohol or benzene, but is mostly converted into the solid modification when distilled at the ordinary pressure; a total conversion is brought about by sodium ethoxide, or by very dilute solutions of sodium hydroxide or carbonate. Both forms of the ester have the normal molecular weight in boiling benzene, and both give the same compound when treated in the cold with alcoholic ammonia solution;

this compound, which has the melting point 168° , as was found by Carrick (Abstr., 1892, 1086), and not 187° , as was stated by Fiquet (Abstr., 1894, i, 32), the author considers to have the constitution $\text{CHPh}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$. By determining the volume of the water formed during the condensation of benzaldehyde and ethyl cyanoacetate, the author finds that the reaction takes place in two stages, the first resulting in the formation of an aldol which then loses water: (1) $\text{Ph}\cdot\text{CHO} + \text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} = \text{OH}\cdot\text{CHPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$; (2) $\text{OH}\cdot\text{CHPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et} = \text{H}_2\text{O} + \text{CHPh}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$.

Acetaldehyde also forms two stereoisomeric ethyl α -cyanocrotonates with ethyl cyanoacetate; with sodium ethoxide, liquid ethyl α -cyanocrotonate is obtained, whilst piperidine gives a viscous syrup, which shows a reddish-green fluorescence, and is probably ethyl α -cyanoisocrotonate.

No stereoisomerides of the following substances could be obtained in this way. Ethyl α -cyano- β -*m*-nitrophenylacrylate, ethyl α -cyano- β -furylideneacrylate, ethyl methylenedioxyphenyl- α -cyanoacrylate, ethyl α -cyano- β -*p*-nitrophenylacrylate, ethyl α -cyano- β -*p*-methoxyphenylacrylate, ethyl α -cyanocinnamylacrylate, or methyl α -cyanocinnamate.

T. H. P.

Triphenylacrylic Acid and Benzhydrol Ether. By HANS STOBBE and OTTO ZEITSCHEL (*Ber.*, 1901, 34, 1963—1968).—When an ethereal solution of benzophenone and ethyl phenylacetate is treated with sodium ethoxide, some benzhydrol ether is formed; this gives a red solution with concentrated sulphuric acid, and when dissolved in a mixture of glacial acetic and sulphuric acids yields benzhydrol acetate. When benzophenone and benzyl cyanide are treated in a similar manner, a small quantity of triphenylacrylonitrile is formed; this dissolves in concentrated sulphuric acid, giving a violet solution.

R. H. P.

Glycerol Monosalicylate. By ERNST TÄUBER (*Ber.*, 1901, 34, 1769—1770).—The insoluble oil produced by passing gaseous hydrogen chloride into a saturated solution of salicylic acid in glycerol at 100° , and described by Göttig (Abstr., 1878, 318) as glycerol monosalicylate, is in reality dichlorohydrin salicylate, $\text{C}_{10}\text{H}_{10}\text{O}_3\text{Cl}_2$ (compare Göttig, Abstr., 1891, 707). *Glycerol monosalicylate*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_3\text{H}_5(\text{OH})_2$, is, however, produced when glycerol and salicylic acid are heated on a water-bath with a small amount of 60 per cent. sulphuric acid; it forms white, microscopic crystals, melts at 76° , is only slightly soluble in water, but very readily so in alcohol, and differs from the dichlorohydrin in that it is miscible with glycerol; it is readily hydrolysed by alkali hydroxides and carbonates.

T. M. L.

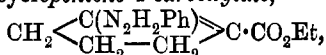
New Synthesis effected by the aid of Compounds containing the Methylene Group attached to one or two Acid Radicles: Action of Epichlorohydrin and Epibromohydrin on the Sodium Derivatives of Benzoyl-acetic Esters. By ALBIN HALLER (*Compt. rend.*, 1901, 132, 1459—1463. Compare

Traube and Lehmann, Abstr., 1899, i, 417).— δ -Chloro- α -benzoyl- γ -valerolactone, $\text{CHBz} \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CH}_2\text{Cl}$, is obtained by treating the sodium derivative of methyl or ethyl benzoylacetate (1 mol.) with epichlorohydrin (1 mol.) in absolute alcohol; it crystallises in needles and melts at $105\text{--}106^\circ$. The corresponding bromo-compound derived from epibromohydrin also crystallises in needles and melts at $92\text{--}93^\circ$. The *phenylhydrazone*, $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2\text{Cl}$, of the chloro-derivative melts at $148\text{--}150^\circ$. δ -Benzoyl- $\alpha\beta$ -butanediol, $\text{CH}_2\text{Bz} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH} \cdot \text{OH}$, results from the action of dilute potassium hydroxide solution on the chloro-lactone, the potassium salts of carbonic, benzoic, and dihydroxyvaleric acid being simultaneously produced; it melts at $90\text{--}91^\circ$, and its semicarbazone at $153\text{--}154^\circ$. G. T. M.

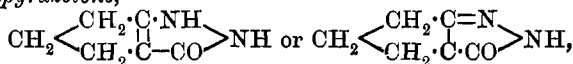
Cyclic β -Ketonecarboxylic Esters. By WILHELM DIECKMANN (*Annalen*, 1901, 317, 27—109. Compare Abstr., 1899, i, 676, 914; 1900, i, 171, 297, 482, 623).—[In part with A. GROENEVELD.]—In these experiments, made with the view of converting the esters of the succinic acid series into β -keto-monocarboxylates, the ethereal salt of the dibasic acid is treated with sodium in the presence of a small amount of absolute alcohol; the resulting *cycloketonic acids* are extracted either with alkalis or by conversion into their copper derivatives, or transformed into the corresponding cyclic ketone by the “ketone hydrolysis” by the action of mineral acids.

The ethyl esters of glutaric, azelaic, and sebacic acids do not yield well-defined products when subjected to this treatment. Ethyl suberate gives rise to an ester of the heptamethylene series which, although not isolated, is identified by conversion into suberone. Ethyl adipate yields ethyl 2-cyclopentanonecarboxylate, which is transformed into cyclopentanone when heated with dilute acid. The hydrolysis of the ester by cold dilute alkalis is a reaction of the first order, the velocity constant being independent of the concentrations of ethereal salt and alkali. The ester, when heated with excess of potassium methoxide in methyl alcohol, is hydrolysed to potassium adipate; with aqueous and alcoholic ammonia, it yields respectively adipamide and *ethyl 2-amino-cyclopentene-1-carboxylate* melting at about 60° ; the latter product is reconverted into the original ester by the action of dilute acids or ferric chloride, the change in the latter case being indicated by the development of a blue coloration.

2-Phenylhydrazinocyclopentene 1-carboxylate,



produced by the action of phenylhydrazine on the β -ketonic ester, melts at 93° , and neither forms a phenylpyrazolone nor develops a coloration with ferric chloride. Hydrazine hydrate, however, yields 3:4-cyclotri-methylenepyrazolone,



which crystallises in lustrous leaflets and melts at $270\text{--}275^\circ$.

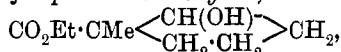
The compound $\text{CO}_2\text{H} \cdot [\text{CH}_2]_3 \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NHPh}$ arises from the interaction of phenylcarbimide and the β -ketonic ester; it melts at

148—150°. The *monoanilide*, $\text{CO}_2\text{H} \cdot [\text{CH}_2]_3 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CO} \cdot \text{NHPh}$ (m. p. 177°), results from the action of 2 mols. of an alkali hydroxide on the preceding compound, excess of the reagent gives rise to carboxyadipic acid, the monoanilide on heating, either alone or in water, loses carbon dioxide and yields the *monoanilide* of adipic acid, the product crystallises in white needles and melts at 152—153°.

The *monophenylhydrazone*, $\text{NHPh} \cdot \text{N} : \text{C} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CO} \end{array} \text{CH}_2$, of 1:2-diketocyclopentane, obtained by adding benzenediazonium chloride to a dilute acid solution of 2-cyclopentanonecarboxylic acid, crystallises in reddish-yellow leaflets, melts at 203°, and yields the diphenylhydrazone on warming with an alcoholic solution of phenylhydrazine; these hydrazones give colour reactions with concentrated sulphuric acid and ferric chloride, the former yielding an indigo-blue and the latter a violet coloration.

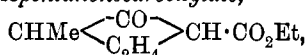
Ethyl 2-cyclopentanolcarboxylate, $\text{CO}_2\text{Et} \cdot \text{CH} \begin{array}{c} \text{CH}(\text{OH}) \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CH}_2$, prepared by the action of 3 per cent. sodium amalgam on an alcoholic solution of the β -ketonic ester, is a colourless oil having a faint odour and boiling at 110—111° under 12 mm. pressure. The *acid* obtained from the ester by hydrolysis with cold potassium hydroxide and decomposition of the *potassium* salt is an uncrystallisable syrup yielding a sparingly soluble *silver* salt and readily losing water to form Δ^1 -cyclopentenecarboxylic acid.

Ethyl 1-methyl-2-cyclopentanolcarboxylate,



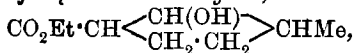
resulting from the reduction of ethyl 1-methylcyclopentanonecarboxylate (compare Abstr., 1900, i, 171), is an oil boiling at 105—110° under 12—15 mm. pressure. The *acid* is uncrystallisable and boils at 160° under 12 mm. pressure; its potassium, zinc, copper, silver, calcium, and barium salts are described.

Ethyl 3-methyl 2-cyclopentanonecarboxylate,



obtained by condensing ethyl α -methyladipate with sodium, boils at 108—109° or at 117—118° under 13 or 20 mm. pressure respectively, closely resembles ethyl 2-cyclopentanonecarboxylate, giving a blue coloration with alcoholic ferric chloride, and a *copper* derivative melting at 166°; "ketone hydrolysis" leads to 3-methylcyclopentane, whilst "acid hydrolysis" furnishes α -methyladipic acid; its velocity constant of alkaline hydrolysis at 12.5° is 0.00144, whilst that of its non-methylated homologue is 0.00126.

Ethyl 3-methyl 2-cyclopentanolcarboxylate,



is a colourless oil boiling at 110—111° under 14 mm. pressure; the *acid* obtained by hydrolysing the ester with potassium methoxide boils at 160° under 12 mm. pressure. The *potassium* and *calcium* salts readily dissolve in water, whilst the *silver* salt is sparingly soluble.

3-Methyl Δ^1 -cyclopentenecarboxylic acid, $\text{CO}_2\text{H}\cdot\text{C} \begin{smallmatrix} \text{CH-} \\ \text{C}_2\text{H}_4 \end{smallmatrix} \text{CHMe}$, obtained by distilling the preceding compound under atmospheric pressure, crystallises in colourless leaflets melting at 42° .

Ethyl 4-methyl-2-cyclopentanonecarboxylate, produced by the condensation of ethyl β -methyladipate, is an oil boiling at $107\text{--}108^\circ$ under 11—12 mm. pressure; its hydrolysis velocity constant at 12.5° is 0.00135. The copper derivative melts at 190° . The ester on "ketone hydrolysis" yields 3-methylcyclopentanone, "acid hydrolysis" furnishes β -methyladipic acid, whilst aqueous ammonia gives rise to β -methyladipamide, and a substance melting at 129° which is probably the amide of 4-methyl-2-cyclopentanonecarboxylic acid; ethyl 2-amino-4-methylcyclopentenecarboxylate results from the action of alcoholic ammonia.

β -Methyl α -isobutyladipic acid, obtained by hydrolysing with baryta water the esters obtained by heating a mixture of ethyl 4-methyl-2-cyclopentanonecarboxylate and isobutyl iodide with alcoholic sodium ethoxide, and distilling the less soluble portion of the product under diminished pressure, is an uncrystallisable syrup boiling at $235\text{--}237^\circ$ under 30 mm. pressure.

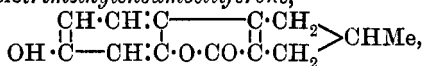
4-Methyl-2-isobutylcyclopentanone, $\begin{smallmatrix} \text{CHMe}\cdot\text{CH}_2 \\ \text{CH}_2\text{---CO} \end{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{CHMe}_2$,

produced by treating an ethereal solution of the preceding ester with calcium oxide, boils at $196\text{--}197^\circ$; it has a faint odour of peppermint, and is optically active, having $[\alpha]_D 62^\circ$. The oxime crystallises in needles and melts at 92° , the semicarbazone melts at $163\text{--}164^\circ$.

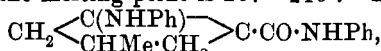
Ethyl 4-methyl-1-isopropyl-2-cyclopentanonecarboxylate, obtained by the action of isopropyl iodide on the sodium potassium derivative of ethyl 4-methyl-2-cyclopentanonecarboxylate dissolved in xylene, is a colourless oil boiling at $130\text{--}131^\circ$ under 15 mm. pressure.

3-Methyl 1-isopropylcyclopentanone, formed by boiling the preceding ester with barium hydroxide solution, is an oil having an odour of menthone, and boiling at 180° ; the semicarbazone melts at 182° .

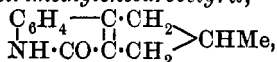
Methyl $\alpha\beta$ -cyclotrimethylenecumbelliferone,



produced by condensing ethyl 4-methyl-2-cyclopentanonecarboxylate with resorcinol in the presence of concentrated sulphuric acid, crystallises with H_2O , and melts at $110\text{--}120^\circ$; when anhydrous, it melts at 180° . Methyl $\alpha\beta$ -cyclotrimethylenedaphnetin is obtained in a similar manner from pyrogallol; it crystallises with H_2O and melts at 120° ; when anhydrous, the melting point is $207\text{--}210^\circ$. The anilide,

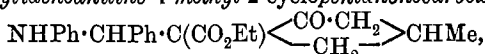


prepared by heating ethyl 4-methyl-2-cyclopentanonecarboxylate with aniline at 150° , crystallises from alcohol in colourless, lustrous prisms and melts at 133° ; when treated with concentrated sulphuric acid, it yields 3:4-methylcyclotrimethylenecarbostyryl,



which melts at 253°, and gives rise to a *hydrochloride* crystallising in lustrous needles.

Ethyl benzylideneaniline 4-methyl-2-cyclopentanonecarboxylate,



prepared by heating together benzylideneaniline and the corresponding ketone ester, melts at 108—110°.

Ethyl 2-*cyclohexanonecarboxylate*, produced by the condensation of ethyl pimelate, has a hydrolysis velocity constant 20 times as great as that of the corresponding 2-*cyclopentanonecarboxylate*; its copper derivative melts at 178°. The ester resembles the corresponding member of the pentamethylene series in its behaviour towards hydrolytic agents; dilute sulphuric acid gives rise to *cyclohexanone*, dilute sodium hydroxide solution liberates the somewhat unstable ketonic acid, whilst excess of potassium hydroxide in methyl alcohol regenerates pimelic acid.

Ethyl Δ¹-tetrahydroanthranilate (*ethyl 2-aminocyclo-Δ¹-hexenecarboxylate*), $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$, is the principal product of the action of aqueous or alcoholic ammonia on ethyl-2-*cyclohexanonecarboxylate*; it crystallises in nacreous leaflets and melts at 74°.

1-*Phenyl-3:4-cyclotetramethylene-5-pyrazolone* [*3-keto-2-phenylhexahydroindazole*], $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} = \text{N} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CO} \end{array} > \text{NPh}$, is produced by mixing together the *cyclohexane* ester and phenylhydrazine either alone or in ethereal solution; it melts at 165°.

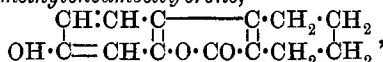
3:4-cyclo*Tetramethylene-5-pyrazolone* [*2-ketohexahydroindazole*] results from the action of hydrazine hydrate on the ketonic ester in alcoholic solution; it melts at 285—286°.

The compound, $\text{CH}_2 \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \right\rangle \text{C}(\text{CO} \cdot \text{NHPh}) \cdot \text{CO}_2\text{Et}$, formed by the interaction of phenylcarbimide on the ketonic ester, melts at 108°; when heated with a methyl alcohol solution of potassium hydroxide, the ring opens, and the acid $\text{CO}_2\text{H} \cdot [\text{CH}_2]_4 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CO} \cdot \text{NHPh}$ is produced; this substance melts at 165°, and when heated above this temperature yields the *monoanilide* of pimelic acid (m. p. 113—114°).

Ethyl 1-methyl-2-cyclohexanonecarboxylate, obtained by methylating the ketonic ester, is an oil boiling at 108—109° under 11—12 mm. pressure; the free acid is somewhat unstable, readily evolving carbon dioxide and becoming converted into 1-methyl*cyclohexanone*. The *phenylhydrazone* of the preceding compound melts at 82°, and when boiled with glacial acetic acid it yields 1-*phenyl-4-methyl-3:4-cyclotetramethylene-5-pyrazolone* [*3-keto-2-phenyl-4-methylhexahydroindazole*] melting at 138°.

Ethyl 1-methyl-2-*cyclopentanonecarboxylate*, when hydrolysed with potassium hydroxide dissolved in methyl alcohol, yields α-methylpimelic acid; ethyl α-methylpimelate is obtained by the action of sodium ethoxide.

1:2-cyclo*Tetramethyleneumbelliferone*,



readily prepared by condensing ethyl 2-cyclohexanonecarboxylate and resorcinol in the presence of concentrated sulphuric acid, is sparingly soluble in the organic solvents, yielding fluorescent solutions; it melts at 203—204°. G. T. M.

Action of Bromine and Chlorine on the Esters of Sodio-diketohydrindenecarboxylic Acid. By L. FLATOW (*Ber.*, 1901, 2145—2149. Compare Abstr., 1900, i, 667).—Ethyl bromodiketohydrindenecarboxylate, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CBr \cdot CO_2Et$, prepared by the action of the calculated quantity of bromine on ethyl sodiodiketohydrindenecarboxylate, suspended in carbon disulphide, forms crystals melting at 72—75°, which decompose in a few days at the ordinary temperature, and suddenly, at 80°, into carbon dioxide and bromodiketohydrindene. By the action of sodium hydroxide, the bromine is replaced by sodium, re-forming the original sodium compound; bromoform is produced at the same time. With potassium iodide, ethyl potassiodiketohydrindenecarboxylate is formed, with the separation of iodine. Bromodiketohydrindene is obtained when ethyl bromodiketohydrindenecarboxylate is boiled in absolute alcohol containing the calculated quantity of water, until the evolution of carbon dioxide ceases (compare Roser and Haselhoff, Abstr., 1888, 1304). Dibromodiketohydrindene is produced from the last-mentioned substance by heating with water until the solution becomes turbid. If the heating is prolonged, trisdiketohydrindene is formed. This compound was also synthesised by the action of sodium ethoxide on a mixture of dibromodiketohydrindene and diketohydrindene, thus confirming the constitution already assigned to it (*loc. cit.*).

Ethyl chlorodiketohydrindenecarboxylate, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CCl \cdot CO_2Et$, prepared by the action of chlorine on an aqueous solution of the sodium compound, crystallises in long, colourless needles melting at 72—74°, and is far more stable than the corresponding bromine compound.

Ethyl hydroxydiketohydrindenecarboxylate, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C(OH) \cdot CO_2Et$, prepared by the action of sodium hydroxide on the chlorine compound, crystallises in needles melting at 120°, dissolves readily in alkalis with a yellow colour, and gives a violet colour with ferric chloride.

K. J. P. O.

3 : 4 : 6-Trichlorophthalic Acid. By CARL GRAEBE and S. ROSTOWZEW (*Ber.*, 1901, 34, 2107—2113. Compare Abstr., 1900, i, 546).—3 : 4 : 6-Trichlorophthalic acid is produced in the manufacture of dichlorophthalic acid, and is separated from the latter by converting the mixed acids into their acid ethyl esters, hydrolysing these compounds into their barium salts, and extracting the latter with hot water, until the final residue corresponds in composition with the formula $C_8HCl_3O_4Ba \cdot H_2O$. The pure trichloro-acid separates from water in prismatic crystals, and is readily soluble in the ordinary organic solvents; at 150—160°, it is completely dehydrated, yielding the anhydride. This compound melts at 148°, sublimes in needles, and, when heated for 2 hours with methyl and ethyl alcohol, yields the

corresponding esters; these substances solidify very slowly, and each consists, probably, of a mixture of two esters; the crystals separating from the methylated product melt at 84—86°, whilst the solid ethyl derivative melts at 89—105°.

The normal ethyl ester, $C_6HCl_3(CO_2Et)_2$, obtained from silver trichlorophthalate, is an oil which does not solidify at -18° .

Dichlorophthalic acid, when boiled for 2 hours with absolute alcohol, yields a mixture of acid and normal esters containing 1.6 per cent. of the latter.

3:4:6-Trichlorophthalimide, $C_6HCl_3\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}NH$, prepared by dissolving the trichloro-acid or its anhydride in concentrated ammonia, crystallises from alcohol in needles melting at 236° ; the acid is readily regenerated by the action of alkali hydroxides.

3:5:6-Trichloroanthranilic acid ($NH_2=2$), is readily obtained when the preceding compound is dissolved in water by the aid of 1 mol. of sodium hydroxide, and treated, first with sodium hypochlorite solution (active Cl = 5.3 per cent.), and then with sodium hydroxide; it crystallises from water and melts at 180° , being therefore isomeric with Beilstein and Kuhlberg's trichloroanthranilic acid (m. p. 210°). When heated at 180° , this trichloro-compound decomposes completely into 2:4:5-trichloroaniline. This result indicates the constitutions of the trichlorophthalic acid, and the trichloroanthranilic acid derived from it.

o-Trichlorobenzoylbenzoic acid ($Cl_3=3:4:6$ or $3:5:6$), results from the condensation of 3:4:6-trichlorophthalic anhydride with benzene in the presence of aluminium chloride; it separates from chloroform in colourless crystals and melts at 177° . This acid dissolves in the ordinary organic solvents and in solutions of the alkali carbonates; it is, however, only sparingly soluble in water.

1:2:4-Trichloroanthraquinone, produced by heating the preceding compound with concentrated sulphuric acid, forms yellow crystals and melts at 185° ; it readily dissolves in benzene or chloroform, but is only sparingly soluble in ether, acetic acid, or alcohol. When fused with alkali hydroxides, the quinone yields phthalic acid.

G. T. M.

isoPropylphthalide. By PIETRO GUCCI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 473—476).—The view that the oily product boiling at 225 — 229° under 160 mm. pressure, obtained by the action of zinc dust on isopropyl iodide and phthalic anhydride (Abstr., 1899, i, 513), is isopropylphthalide, is confirmed by an examination of the compounds it yields with sodium hydroxide, which are found to be sodium benzoate and isobutyrate. The identity of the compound with Roser's isopropylphthalide (Abstr., 1885, 268) is also established, and hence the correctness of the constitution assigned to the latter product.

T. H. P.

Benzylated Ethyl Acetonedicarboxylates. By FRITZ FICHTER and HEINRICH SCHIESS (*Ber.*, 1901, 34, 1996—2001).—The product of the action of sodium ethoxide on benzyl chloride and ethyl acetonedicarboxylate contains the esters of mono-, di-, and tri-benzylacetonedicarboxylic acids; the tribenzyl derivative, $C_{30}H_{32}O_6$, was isolated in

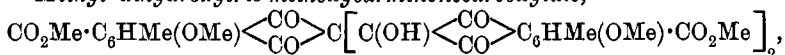
glistening needles melting at 82°, and is perhaps identical with the substance melting at 92° which von Pechmann and Dünschmann (Abstr., 1891, 674) described as a dibenzyl derivative. When hydrolysed with alkalis, it gives benzylmalonic acid, and dibenzylacetic acid and its *ethyl* ester; the latter, $C_{18}H_{20}O_2$, crystallises from dilute alcohol in large prisms and melts at 88—89°.

By reducing with aluminium amalgam a crude mixture of esters containing the monobenzyl ester, *β*-hydroxybenzylglutaric acid, $C_{12}H_{14}O_5$, has been prepared; it crystallises from a mixture of ether and light petroleum, melts at 126—128°, and gives a crystalline *barium* salt.

T. M. L.

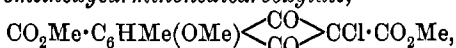
Carminone Compounds. By CARL LIEBERMANN and JOSEF LANDAU (*Ber.*, 1901, 34, 2153—2163. Compare Abstr., 1900, i, 661).—The name “carminone” is suggested for 5-hydroxy-7-methyldiketohydrindene, and “carminonecarboxylic acid” for 5-hydroxy-7-methyldiketohydrindene-4-carboxylic acid. It is found that the tetramethyl derivative of cochinelic acid is best prepared by heating the acid (1 mol.) with silver oxide (3—4 mols.) and excess of methyl iodide at 100° (compare *loc. cit.*).

Methyl dihydroxytris-methoxycarminonecarboxylate,

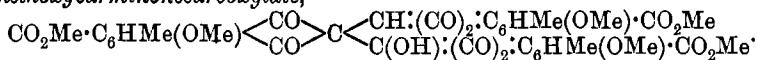


prepared by the action of iodine on methyl sodiomethoxycarminonedicarboxylate, forms a white powder decomposing at 175°, and dissolves in alkalis with a yellow colour which rapidly becomes deep red in the air. From the red solution, acids throw down a red precipitate (compare this vol., i, 552).

Methyl chloromethoxycarminonedicarboxylate,

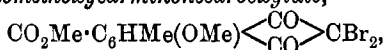


prepared by the action of chlorine on the sodium derivative, crystallises in colourless needles melting at 165—166°, and decomposes when boiled with water with elimination of hydrogen chloride. The corresponding *bromine* derivative forms needles melting at 168—170°, and is far less stable than the chlorine compound. With sodium iodide, it yields the sodium compound just mentioned. When boiled with aqueous methyl alcohol, the bromine derivative is converted into a compound decomposing at 275—276°, which is probably *methyl hydroxytris-methoxycarminonecarboxylate*,



Hydroxytris-methoxycarminonecarboxylic acid, prepared by hydrolysing the last-mentioned substance with potassium hydroxide, exists in a deep red and a pale yellow modification. Acetone converts the former into the latter, and alkalis induce the reverse change.

Methyl dibromomethoxycarminonecarboxylate,



prepared by brominating methyl bromomethoxydicarboxylate, crystallises in colourless needles melting at 141—143°, which liberate

iodine from sodium iodide, and lose both bromine atoms when treated with aqueous methyl alcohol or silver oxide; the two bromine atoms are therefore not in the benzene nucleus.

α -Bromocarmin (2:2:4:6-tetrabromocarminone), when boiled with aqueous sodium carbonate, yields bromoform, dibromohydroxyhomophthalic acid, and a colouring matter which exists in a red and a colourless form; the latter is converted into the former by alkalis. The composition of this substance could not be fixed, but it has lost two of the four bromine atoms present in α -bromocarmin.

Dibromodiethoxycarminone, $\text{OH} \cdot \text{C}_6\text{Br}_2\text{Me} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}(\text{OEt})_2$, prepared from α -bromocarmin by the action of alcohol in the presence of silver oxide, crystallises in yellow needles melting at 182 – 184° , and dissolving in alkalis with a yellow colour. K. J. P. O.

Secondary Products of the Action of Sulphuric Acid on Wood Charcoal. By AUGUSTE VERNEUIL (*Compt. rend.*, 1901, 132, 1340–1343. Compare Abstr., 1894, i, 217).—Benzenepentacarboxylic acid, separated by fractional precipitation with barium hydroxide from the product of the action of sulphuric acid on wood charcoal, exhibits a distinct, greenish-yellow phosphorescence lasting about 6 seconds. This effect is due to an impurity, for the colourless crystals of the compound obtained from its purified lead salt by decomposition with hydrogen sulphide are devoid of this property. These crystals do not contain $6\text{H}_2\text{O}$, as formerly supposed, but have the composition $\text{C}_6\text{H}(\text{CO}_2\text{H})_5 \cdot 5\text{H}_2\text{O}$; they crystallise in the rhombic system, and have a very well marked double refraction and high dispersive power.

Pyromellitic acid has also been isolated from the products of the action of sulphuric acid on wood charcoal, the yield amounting to 2 per cent. It crystallises from water with 2 mols. of the solvent, and is readily separated from benzenepentacarboxylic acid on account of its slight solubility. Besides mellitic acid, no other crystalline compounds have been isolated from the products of this action. The charcoal employed had the following composition, C, 87.62; H, 2.55; O, 8.38; ash, 1.43, the excess of hydrogen over the amount required by the oxygen to form water being 1.51.

There is undoubtedly some connection between the presence of the hydrogen and the formation of the benzenoid acids, for this wood charcoal, after being calcined at a bright red heat, is only very slowly attacked by sulphuric acid, and does not yield mellitic or benzenepentacarboxylic acid. G. T. M.

Compounds from Lichens. By WILHELM ZOFF (*Annalen*, 1901, 317, 110–145. Compare Abstr., 1895, i, 297; 1896, i, 103; 1897, i, 255, 362, 436; 1898, i, 89, 489; 1899, i, 716).—*Placodium alphonacum* contains salazinic acid but not psoromic acid as previously suggested. *P. crassum* contains a relatively large amount of usnic acid, and a very small quantity of psoromic acid; this is invariably true, whatever be the habitat of the lichen.

The crystalline yellowish-green and colourless acids derived from *P. gypsaceum* and *P. Lagascae* are usnic and psoromic acid respectively,

the latter being identified by conversion into parellinic acid (m. p. 230°), by heating with aqueous sodium hydroxide solution.

The thallus of *P. fulgens* yields parietin and a colourless substance which is neither usnic nor psoromic acid.

Pachnolepia decussata, when extracted with ether, yields a mixture of crystalline substances containing atranoric and lecanoric acids, and a small amount of a compound crystallising in prisms insoluble in potassium hydroxide solution, and not reddened by calcium hypochlorite.

Sticta aurata, whether grown in France or in the Transvaal, yields about 5.5–6 per cent. of stictaurin; this substance forms the yellow colouring matter of *S. flavicans*, *S. crocata*, *S. impressa*, and *S. orygmæa*. The last-named lichen contains, in addition, a new acid, *orygmæanic acid*, crystallising in brown, monoclinic plates or prisms and melting at 310° . The solutions of this acid in organic solvents have a red colour; in alkaline solutions it dissolves, giving a violet coloration; its sodium, calcium, and barium salts are described.

Parmelia locarnensis yields gyrophoric acid and a new substance, *imbricatic acid*, melting at $103\text{--}104^{\circ}$; in melting point, this acid resembles rangiformic and atranoric acids, differing from the former, however, in developing a violet coloration with ferric chloride, and from the latter in being precipitated from its ethereal solution on the addition of potassium carbonate.

Diffusin, which was formerly obtained from *Parmelia diffusa*, also exists in *P. sorediata*; the two specimens agree in all respects, and are totally different from lecanoric acid, also stated by Hesse to exist in *P. sorediata*.

Lobaric acid, derived from *Parmelia omphalodes*, melts at $192\text{--}193^{\circ}$, has the composition $C_{24}H_{26}O_8$, and is identical with the author's stereocaulic acid (Abstr., 1896, i, 103) and Hesse's usnetic acid; it has already been extracted from nine species of lichens.

Divaricatic and usnic acids are always found together in specimens of *Evernia divaricata* grown in different localities.

Umbilicatic acid, found in *Gyrophora polyphylla*, is accompanied by gyrophoric acid.

Alectoria cana develops an intense yellow coloration with sodium hydroxide solution, which is not given by the allied species, *A. implexa*; the former lichen yields salazinic acid, whilst the latter does not. Hesse, who had probably confounded these two species, states that *A. cana* contains alectoric acid, but no salazinic acid.

The yellow colouring matter in the rare *Pertusaria lutescens* is probably thiophaninic acid, $C_{12}H_6O_8$, obtained from thiophanic acid by Hesse by the action of hydrogen iodide.

Mallotium Hildenbrandii has not hitherto yielded any lichen acids, but only a small quantity of a crystalline substance of the phytosterol type.

G. T. M.

Chemical Action of Light. II. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1901, 34, 2040–2046. Compare this vol., i, 329).—When *o*-nitrobenzaldehyde is exposed to light, either in

solution in benzene, ether, or acetone, or as a thin, crystalline layer obtained by moistening the inside of a flask with its benzene solution and allowing the solvent to evaporate, it is converted into *o*-nitrosobenzoic acid. In methyl alcoholic solution, *methyl o-nitrosobenzoate* is obtained, separating in colourless, rhombic plates melting at 152—153° to an emerald green liquid. *Ethyl o-nitrosobenzoate*, obtained by the action of light on an alcoholic solution of *o*-nitrobenzaldehyde, is deposited in well-formed, colourless crystals melting at 120—121° to an emerald green liquid. In isopropyl alcoholic solution, the action of light on *o*-nitrobenzaldehyde yields *o*-nitrosobenzoic acid, whilst in paraldehyde solution, together with this acid, a small quantity of a neutral compound, $C_9H_7O_3N$, is formed, which gives colourless solutions and separates from alcohol in large, colourless prisms melting at 121° to a colourless liquid; it reduces ammoniacal silver solution and does not give an indigo-blue coloration when boiled with alkali.

The action of light on solutions of *m*- and *p*-nitrobenzaldehyde gave no definite products. T. H. P.

Oxidation of Aromatic and Aliphatic Aldoximes. By EUGEN BAMBERGER and THOR SCHEUTZ [in part with R. SELIGMANN] (*Ber.*, 1901, 34, 2023—2033).—Benzonitrile is found amongst the products of oxidation of benzaldoxime by permonosulphuric acid (Caro's reagent; *Abstr.*, 1900, i, 500). Under similar conditions, anisaldoxime gives anisaldehyde, anisic acid, anisonitrile, anishydroxamic acid, and anisylnitromethane. *Anisylnitromethane*, $OMe \cdot C_6H_4 \cdot CH_2 \cdot NO_2$, is a pale yellowish oil, which readily distils in a current of steam, and dissolves completely when shaken with alkali hydroxides; it shows Konowaloff's reaction, and its alkaline solution deposits a violet-brown ferric salt when mixed with ferric chloride. *Anisylnitroformaldehydephenylhydrazone*, $OMe \cdot C_6H_4 \cdot C(NO_2) : N_2HPh$, prepared by the action of phenyldiazonium acetate on the preceding compound, crystallises from alcohol in glistening, red needles, melts with liberation of gas at 114° (corr.); it dissolves in dilute alkali hydroxides, but concentrated sodium hydroxide precipitates the sodium salt in needles with a bronze-like lustre.

m-Nitrobenzaloxime gives *m*-nitrobenzhydroxamic acid, *m*-nitrobenzoic acid, and a substance, $C_{14}H_8O_5N_4$, which is probably *dinitrodi-benzenylazoxime*, $N \begin{smallmatrix} \diagup C(C_6H_4 \cdot NO_2) \cdot O \\ \diagdown C(C_6H_4 \cdot NO_2) : N \end{smallmatrix}$. The latter crystallises from alcohol in pale yellowish needles and melts at 147.5—149.5°; *m*-nitrobenzamide, *m*-nitrobenzonitrile, and *m*-nitrophenylnitromethane could not be detected.

p-Nitrobenzaloxime gives *p*-nitrobenzhydroxamic acid, but the oxidation has not been further studied.

Acetaldoxime gives chiefly acetic acid, but acethydroxamic acid, nitroethane, and acetonitrile are also produced.

Propaldoxime gives prophydroxamic acid and a small amount of nitropropane.

Valeraldoxime gives valerhydroxamic acid and a small amount of nitropentane; *valerhydroxamic acid*, $CHMe_2 \cdot CH_2 \cdot C(OH) : NOH$, melts

at 73.5—76°, crystallises in white, pearly flakes or flat needles, and, unlike most hydroxamic acids, is readily soluble in ether.

*iso*Butyraldoxime gives *isobutyryl*hydroxamic acid and nitrobutane.

T. M. L.

Action of Sodium Ethoxide on Mixtures of Ketones and Ethyl Malonate. By HANS STOBBE [and in part GEORG HEUN] (*Ber.*, 1901, 34, 1955—1962).—When a mixture of acetone and ethyl malonate is treated with sodium ethoxide suspended in ether, the principal products obtained are ethyl dimethyldihydroresorcyate and dimethyldihydroresorcinol. Benzophenone, when treated in a similar manner, yields diphenylcarbinol; acetophenone yields benzoic acid, a compound, $C_{24}H_{18}O$, which melts at 183°, phenylmethylcarbinol, and a hydrocarbon, $C_{16}H_{14}$, which crystallises in large plates or prisms, and melts at 131—132°. In these cases, the sodium ethoxide appears to have acted as a reducing agent.

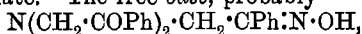
R. H. P.

ω -Halogenacetophenone Oximes. By H. KORTEN and ROLAND SCHOLL (*Ber.*, 1901, 34, 1901—1910).—The view which has been several times put forward that α -halogen ketones containing the grouping $\cdot CO \cdot CHCl$ are converted by hydroxylamine directly into glyoximes without the formation of intermediate products was shown by Scholl and Mathaiopoulos (*Abstr.*, 1896, i, 520) to be erroneous in the case of aliphatic compounds which under suitable conditions yield α -halogenketoximes. The authors find that analogous compounds can be obtained in the aromatic series if the hydroxylamine be made to act in presence of a mineral acid. In this way, ω -halogenacetophenones yield aromatic α -halogenketoximes, which are readily crystallisable compounds belonging to the *syn*-phenyl series. When the hydroxylamine is employed in alkaline solution, the glyoxime obtained is accompanied by a small proportion of the *anti*-phenyl ketoxime. The halogen of these α -halogenketoximes readily reacts with alkalis and ammonia, the latter yielding tertiary amines which, under the action of alcoholic hydrochloric acid, are partially de-oximated and transformed into paroxazine derivatives.

syn-Phenylchloromethylketoxime, $\begin{array}{c} Ph \cdot C \cdot CH_2Cl \\ | \\ OH \cdot N \end{array}$, obtained by the in-

teraction of ω -chloroacetophenone (1 mol.) and hydroxylamine hydrochloride (3 mols.) in aqueous methyl alcoholic solution at the ordinary temperature, separates from carbon disulphide in crystals melting at 88.5—89°. Its vapours are very painful to the eyes, whilst when placed on the skin in either the solid or dissolved state, it produces a very persistent burning sensation. When it is treated with phosphorus pentachloride in ethereal solution, and the product decomposed with water, chloroacetanilide is obtained. With phenylcarbimide, it yields *carbanilidosynphenylchloromethylketoxime*, $CH_2Cl \cdot CPh : N \cdot O \cdot CO \cdot NHPh$, crystallising from light petroleum in colourless needles melting at 118—120°, and with acetic anhydride, the *acetyl* derivative, $CH_2Cl \cdot CPh : N \cdot OAc$, separating from light petroleum in needles melting at 67—68°, is obtained. With concentrated ammonia solution in the cold, the oxime gives

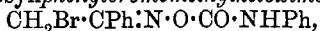
Trihydroxyiminotriphenacylamine, $N(CH_2 \cdot CPh \cdot N \cdot OH)_3$, which forms shining leaflets melting and decomposing at 222° ; it is readily soluble in sodium hydroxide solution, and is reprecipitated by dilute acids. With hot concentrated hydrochloric acid, it yields *two hydrochlorides*, (1) a colourless compound, $C_{24}H_{22}O_6N_3 \cdot 2HCl \cdot H_2O$, crystallising from acetic acid in shining, white leaflets melting at 242° ; its solution in concentrated sulphuric acid becomes dark blue on heating, whilst on cooling and adding water it changes first to violet, then to rose red, and finally loses its colour, and gradually deposits colourless needles, possibly of a sulphate. The free *base*, probably



corresponding with this hydrochloride crystallises from dilute alcohol in yellowish needles melting at 92° . (2) A yellow salt, $C_{24}H_{20}O_2N_2 \cdot HCl$, separating from alcohol in small, yellow crystals melting and decomposing at 208° ; it dissolves in the ordinary organic solvents except ether and light petroleum, and when heated with concentrated sulphuric acid gives a reddish-yellow solution. The free *base*, probably $O \begin{smallmatrix} \diagup CPh \cdot CH \\ \diagdown CPh \cdot CH \end{smallmatrix} N \cdot CH_2 \cdot CPh \cdot NOH$, is deposited from dilute alcoholic solution in yellowish-red crystals melting at 191° ; the dilute alcoholic solution exhibits a yellowish-red fluorescence, and dyes animal fibres a yellowish-red colour.

syn-Phenylbromomethylketoxime, $\begin{smallmatrix} Ph \cdot C \cdot CH_2Br \\ | \\ OH \cdot N \end{smallmatrix}$, obtained, together

with a small proportion of the *anti*-compound as a mixture melting at 92° , when *o*-bromoacetophenone (1 mol.) and hydroxylamine hydrochloride (3 mols.) react in aqueous methyl alcoholic solution at the ordinary temperature, separates from light petroleum in crystals melting at 89.5° ; it dissolves readily in the ordinary organic solvents, and when placed on the skin, especially in solution, it causes a burning feeling, whilst its vapours vigorously attack the eyes. The oxime melting at 92° , when treated with phosphorus pentachloride in ethereal solution and afterwards with water, gives monobromoacetanilide. *Carbanilinosynphenylbromomethylketoxime*,



crystallises from a mixture of benzene and light petroleum in silky needles melting at $120-121^\circ$. *Acetylsynphenylbromomethylketoxime*, $CH_2Br \cdot CHPh \cdot N \cdot OAc$, melts at $74-75^\circ$. The action of ammonia on *o*-bromoacetophenoneoxime yields the trihydroxyiminotriphenacylamine melting at 222° .

anti-Phenylbromomethylketoxime, $\begin{smallmatrix} Ph \cdot C \cdot CH_2Br \\ | \\ N \cdot OH \end{smallmatrix}$, when crystallised

from light petroleum, melts at $96.5-97^\circ$; when kept, it decomposes and turns yellow.

syn-m-Nitrophenylbromomethylketoxime, $\begin{smallmatrix} NO_2 \cdot C_6H_4 \cdot C \cdot CH_2Br \\ | \\ OH \cdot N \end{smallmatrix}$, *crys-*

tallises from a mixture of benzene and light petroleum in yellowish needles melting at $126.5-127^\circ$; it has practically no action on the skin or eyes, and is much more stable than the non-nitrated derivative. When treated with phosphorus pentachloride in ethereal solution, and

afterwards with water, it yields *m*-nitrobromoacetanilide. *Carbanilino-m-nitro-ω-bromoacetophenoneoxime*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{CH}_2\text{Br}) : \text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$, separates from a mixture of benzene and light petroleum in yellowish needles melting at $145-146^\circ$. *Acetyl-m-nitro-ω-bromoacetophenoneoxime*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{CH}_2\text{Br}) : \text{N} \cdot \text{OAc}$, crystallises from a mixture of light petroleum and benzene in yellowish needles melting at $64-65^\circ$.

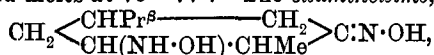
T. H. P.

Auto-oxidation of Carvone. By CARL D. HARRIES (*Ber.*, 1901, **34**, 2105—2106).—When carvone, barium hydroxide, and methyl alcohol are shaken for some considerable time in contact with oxygen, the ketone slowly dissolves, and the solution then contains barium peroxide and 1-methyl-4-propenyldihydroresorcinol formed in accordance with the following equation, $\text{C}_{10}\text{H}_{14}\text{O} + \text{H}_2\text{O} + \text{O}_2 = \text{H}_2\text{O}_2 + \text{C}_{10}\text{H}_{14}\text{O}_2$; this diketone is identical with the product obtained by oxidising hydroxylaminocarvoxime (compare Abstr., 1898, i, 568; 1899, i, 583). The diketone is accompanied by a small amount of a product having the odour of strawberries which has not been investigated.

G. T. M.

Δ^6 -Menthene-2-one and Carvotanacetone. By CARL D. HARRIES (*Ber.*, 1901, **34**, 1924—1935).—Carvotanacetone is the racemic form of the ketone $\text{CH}_2 \begin{smallmatrix} \text{CHPr}^\beta \cdot \text{CH}_2 \\ \text{CH} = \text{CMe} \end{smallmatrix} \text{CO}$ (compare Semmler, Abstr., 1900, i, 676), and the dihydrocarvone now obtained by the reduction of hydrobromocarvone is its optically active modification.

[With CARL STIRM.]—When hydrobromocarvone dissolved in methyl alcohol is reduced with zinc dust, about one-quarter of the product is carvone, and the remainder is Δ^6 -menthene-2-one; this is a bright yellow, strongly refractive oil, which boils at $227-228^\circ$, or at $96-97^\circ$ under 9 mm. pressure, has a sp. gr. 0.9411 at 10° and 0.9351 at 19° , and in a 10 cm. tube at 25° has $n_D + 49.5^\circ$. The semicarbazone crystallises in plates, sinters at 170° , and melts at $173-174^\circ$; the compound with hydrogen sulphide, $2\text{C}_{10}\text{H}_{16}\text{O}, \text{H}_2\text{S}$, crystallises in lustrous needles and melts at $222-225^\circ$; the oxime crystallises in large prisms and melts at $75-77^\circ$. The oxaminoxime,



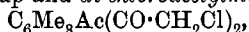
obtained when the ketone remains for eight days with an alcoholic solution of hydroxylamine, crystallises with $\frac{1}{2}\text{H}_2\text{O}$ in felted needles, which sinter at 90° and melt at $95-97^\circ$, forms an oxalate melting at $130-135^\circ$, and when oxidised slowly by a current of air yields the dioxime, $\text{CH}_2 \begin{smallmatrix} \text{CHPr}^\beta \text{---} \text{CH}_2 \\ \text{C} : (\text{N} \cdot \text{OH}) \cdot \text{CHMe} \end{smallmatrix} \text{C} : \text{N} \cdot \text{OH}$, which crystallises in colourless prisms and melts at $194-196^\circ$, when it decomposes. When reduced with zinc dust and an alcoholic solution of sodium hydroxide, the ketone yields *d*-carvomethone and when reduced with aluminium amalgam, a dimolecular compound, $\text{C}_6\text{H}_7\text{MePr}^\beta\text{O} \cdot \text{C}_6\text{H}_7\text{MePr}^\beta\text{O}$, which is a syrup, but yields a phenylhydrazone melting at 260° . The ketone slowly combines with hydrogen bromide, forming a yellow oil, which, when treated with lead nitrate, yields the original compound.

The semicarbazone obtained from Semmler's carvotanacetone

(*loc. cit.*) melted at 177° , and the oxaminoxime sintered at 155° and melted at about 162° . This oxaminoxime could not be obtained quite pure, and it is probable that "carvotanacetone" is a mixture of the racemic form of the ketone (dihydrocarvone) with other compounds.

R. H. P.

1:3:5-Triacylated Benzenehydrocarbon and some Compounds of Di-chloroacetylmesitylene. By FRANZ KUNCKELL and A. HILDEBRANDT (*Ber.*, 1901, 34, 1826—1829).—When acetylmesitylene is treated with chloroacetyl chloride and aluminium chloride in sunlight, the two remaining hydrogen atoms of the nucleus are replaced by the chloroacetyl group and *di-chloroacetylmesitylene*,



is produced, which forms white, compact crystals melting at 130° . It has not, however, been found possible to replace the three hydrogen atoms by either the acetyl or chloroacetyl group.

Dinitro-2:4:6-trimethylbenzoic acid, $\text{C}_6\text{Me}_3(\text{NO}_2)_2\cdot\text{CO}_2\text{H}$, formed by the action of nitric acid on di-chloroacetylmesitylene, crystallises in long, white needles melting at 230 — 231° . The *chloride* crystallises in white needles melting at 154 — 155° ; the *anilide* crystallises in white needles melting at 300 — 310° ; and the *phenylhydrazide* forms white needles melting above 300° . Di-chloroacetylmesitylene is converted by bromine into a crystalline compound melting at 162 — 163° , which has the formula $\text{C}_{13}\text{H}_9\text{O}_2\text{Cl}_2\text{Br}_5$, but the constitution of which has not yet been ascertained. When treated with phenylhydrazine in benzene solution, it yields *di-chloroacetylbromomesitylene*, which crystallises in white, lustrous plates melting at 113° .

A. H.

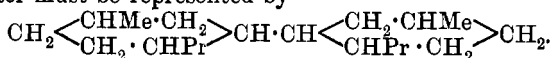
Hydroxytris-diketohydrindene. By CARL LIEBERMANN and JOSEF LANDAU (*Ber.*, 1901, 34, 2149—2152. Compare *Abstr.*, 1900, i, 667).—Hydroxytris-diketohydrindene, $\text{C}_{27}\text{H}_{14}\text{O}_7$, is formed when a solution of tris-diketohydrindene in potassium hydroxide is boiled with free access of air. The initially colourless solution becomes deep red; from this, acids precipitate the hydroxy-compound as a deep red powder melting and decomposing at 218 — 219° , and readily soluble in warm water or chloroform. By recrystallisation from acetic acid, it is transformed into a colourless or faintly yellow, isomeric acid, which crystallises in leaves melting and decomposing at 225 — 228° , insoluble in water or chloroform. The yellow modification is immediately transformed into the red by dissolving in alkalis, ammonia, or pyridine. The formula $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH}:(\text{CO})_2:\text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{C}(\text{OH}):(\text{CO})_2:\text{C}_6\text{H}_4 \end{smallmatrix}$ is suggested for one of the acids.

From the colourless solution of tris-diketohydrindene in potassium hydroxide, acids precipitate tris-diketohydrindene unchanged. On boiling a solution in some excess of alkali without access of air, red needles separate which proved to be *isoethinedipthalide* (Gabriel and Leupold, *Abstr.*, 1898, i, 481 and 482).

The golden-yellow potassium and the red barium salts, previously described (*Abstr.*, 1900, i, 667), are shown to be derivatives of hydroxytris-diketohydrindene, and to have respectively the formulæ $\text{C}_{27}\text{H}_{12}\text{O}_7\text{K}_2$ and $\text{C}_{27}\text{H}_{12}\text{O}_7\text{Ba}$.

K. J. P. O.

Haloid Derivatives of Menthol, and Hydrocarbons derived from them. By NICOLAI KURSANOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 289—302).—When menthyl chloride, obtained by the action of phosphorus pentachloride on menthol in light petroleum solution, is dissolved in ether and the solution boiled with an excess of sodium, it gives rise to menthene, menthane, and two dimenthyls, $C_{20}H_{38}$, one of which is a liquid. The other *dimenthyl*, which dissolves readily in ether or benzene, and to a slight extent in alcohol, crystallises from hot alcohol in drusy masses, and from cold alcohol or benzene in well-developed, many-faced crystals which melt at $105.5-106^\circ$, and boil at $185-186^\circ$ under 21 mm. pressure; it has the normal molecular weight in freezing benzene, and in a 19.4 per cent. benzene solution $[\alpha]_D -51.18'$. The same products, namely, menthene, menthane, and liquid and crystalline dimenthyls, are obtained on boiling with sodium, ethereal solutions of the menthyl chloride and iodide, obtained by heating the corresponding haloid hydracids with menthol. It has been found by various investigators that when menthyl chloride is boiled with alcoholic potassium hydroxide, it is partly decomposed, the remainder differing from the original by possessing a considerable lævo-rotatory power. By pushing the action of the alcoholic potassium hydroxide until the menthyl chloride remaining is no longer decomposed, a lævo-modification having constant properties and quite free from menthene is obtained; the same menthyl chloride may also be prepared by boiling the ordinary chloride with aniline. It has $[\alpha]_D -50.56'$ and a sp. gr. 0.9555 at $0^\circ/0^\circ$, 0.9411 at $20^\circ/0^\circ$, and 0.943 at $15^\circ/15^\circ$; it boils at $109-110^\circ$ at 30 mm. pressure. Slawinski (*loc. cit.*) gave for this compound $[\alpha]_D -51.57'$, the sp. gr. 0.941 at 18° , and the boiling point $91-93^\circ$ under a pressure of 13.5 mm. The homogeneity of this menthyl chloride is indicated by the fact that, when boiled in ethereal solution with sodium, it yields as sole product the crystalline dimenthyl described above. The optical activity of the menthyl chloride and of the dimenthyl derived from it shows that both these compounds must be of a secondary nature, and the formula of the latter must be represented by



Kondakoff and Lutschinin (*Abstr.*, 1900, i, 104) supposed that the action of hydriodic acid on menthol yields tertiary menthyl iodide, but the formation of some crystalline dimenthyl when it is boiled in ethereal solution with sodium shows that some secondary compound is present. For preparing the tertiary halogen compound, the author uses von Baeyer's method of acting on an acetic acid solution of menthene with the halogen hydracid. The menthyl bromide thus obtained boils at $98-100^\circ$ under 11—12 mm. pressure, and has the sp. gr. 1.167 at $15^\circ/15^\circ$ and 1.1663 at $20^\circ/0^\circ$, Kondakoff (*Abstr.*, 1895, i, 549) giving the boiling point $100-103^\circ$ under 13 mm. pressure, and the density as 1.179 at 0° and 1.161 at 23° ; it has a slight dextrorotation, due, possibly, to admixture with a small quantity of menthene. This tertiary menthyl bromide, as also the tertiary chloride obtained in a similar way, when boiled in ethereal solution with sodium, yields a practically inactive dimenthyl.

The author considers that the liquid dimethyl just mentioned is probably a stereoisomeride of the crystalline compound.

Ethylmenthane, $\text{CH}_2 \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHPr} \end{smallmatrix} \text{CHEt}$, prepared by the action of zinc ethyl on *l*-menthyl chloride, boils at 209—210° under 730 mm. pressure, has the sp. gr. 0.8275 at 0°/0°, 0.8146 at 20°/0°, and 0.8159 at 20°/20°, $[\alpha]_D -12^\circ 15'$, and is the first optically active naphthene obtained. T. H. P.

Action of Nitric Anhydride on Camphene. By NICOLAUS I. DEMJANOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 283—289).—The action of nitric anhydride on a chloroform solution of camphene yields an acid, $\text{C}_{10}\text{H}_{15}\text{O}_5\text{N}$, which separates from aqueous alcohol in long prisms, often grouped together in spherical aggregates, or in short, stout prisms melting at 140—141°, and swelling up, turning brown, and evolving gas at 165—170°; it decomposes potassium carbonate, giving a soluble potassium salt, and has the normal molecular weight in freezing acetic acid. The sparingly soluble *silver* salt was analysed. When reduced by means of tin and hydrochloric acid, or when heated with a concentrated aqueous solution of potassium hydroxide, the acid is converted into dehydrocamphenylic acid.

The first action of nitric anhydride on camphene is probably the formation of the nitric ester of camphene glycol, $\text{C}_{10}\text{H}_{16}\text{O}_5\text{N}_2$, which is afterwards transformed into the acid, $\text{C}_8\text{H}_{14} \cdot \text{C}(\text{O} \cdot \text{NO}_2) \cdot \text{CO}_2\text{H}$, melting at 140—141°, just described. These results, together with those of the action of nitric acid and of nitrous anhydride on camphene, lend support to Wagner's formula, $\text{C}_8\text{H}_{14} \cdot \text{C} \cdot \text{CH}_2$, for camphene. T. H. P.

The Sugar obtained from Cerebrin. By FRIEDRICH N. SCHULZ and FRITZ DITTHORN (*Zeit. physiol. Chem.*, 1901, 32, 425—427. Compare Abstr., 1890, 121).—It has been proved beyond doubt that the sugar obtained by the hydrolysis of cerebrin with sulphuric acid is galactose and not a galactosamine. J. J. S.

Chlorophyll. Degradation of Phyllocyanin to Hæmopyrrole. By MARCELLUS NENCKI and LEO MARCHLEWSKI (*Ber.*, 1901, 34, 1687—1690).—When phyllocyanin, in the form of its copper acetate salt, is reduced with hydriodic acid and phosphonium iodide, it yields hæmopyrrole (this vol., i, 434), which was isolated in the form of its mercurichloride. This fact confirms the close relationship of hæmatoporphyrin and phylloporphyrin. W. A. D.

Oxidation of Melaninic Acid. By WALTER JONES and JOHN AUER (*Amer. J. Physiol.*, 1901, 5, 321—332).—Melaninic acid, obtained from the black pigment of horse-hair, was oxidised by means of potassium permanganate. Oxalic acid was found to be one of the principal end-products. No aromatic substance was found. The pigment is probably related to the proteids, but the predominant grouping in it is that which in the proteids gives rise to aliphatic amino-acids. W. D. H.

Dehydromucic Acid. By HENRY B. HILL (*Amer. Chem. J.*, 1901, 25, 440—445).—This paper is an introduction to the two following.

On reducing dehydromucic acid with sodium amalgam, Seelig (Abstr., 1879, 783) obtained two isomeric acids, $C_6H_6O_5$; although, as has been stated by Schrötter (Abstr., 1888, 1060), the acid of lower melting point or α -acid is the only direct product of reduction, it has not been found possible to avoid its partial conversion into that of higher melting point, the β -isomeride. The α -acid, being the first product of reduction, must have the structure $\begin{array}{c} \text{CH}\cdot\text{CH}(\text{CO}_2\text{H}) \\ | \\ \text{CH}\cdot\text{CH}(\text{CO}_2\text{H}) \end{array} > \text{O}$, and the β -acid has probably

the same constitution, since it is unstable in alkaline solution; the author considers that the former acid is the *cis*-form, whilst the latter is the inactive combination of the two active *cis-trans*-modifications. Both acids are optically inactive; the β -acid has been resolved into two optically active constituents by means of their cinchonine salts.

The γ -acid, which is the final product of the action of alkalis on the α - or β -acid, has the configuration $\begin{array}{c} \text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H}) \\ | \\ \text{CH}=\text{C}(\text{CO}_2\text{H}) \end{array} > \text{O}$, and can be separated into two optically active components. E. G.

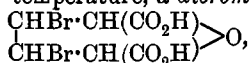
Dehydromucic Acid and certain of its Derivatives. By ISAAC K. PHELPS and WILLIAM J. HALE (*Amer. Chem. J.*, 1901, 25, 445—463).—Dehydromucic acid is obtained in a yield of 34·6 per cent., by heating potassium hydrogen saccharate with hydrobromic acid of sp. gr. 1·56 for 16 hours, whilst by the action of hydrobromic acid of sp. gr. 1·49 on mucic acid, a yield of 20·2 per cent. is produced. The statement of Schmidt and Cobenzl (Abstr., 1884, 1125), that the acid could be obtained by the action of heat on potassium mucate, could not be confirmed. Dehydromucic acid is soluble in water at 18° to the extent of 0·1 per cent., the barium salt 0·91 per cent., and the calcium salt 3·94 per cent.; the *potassium* salt crystallises with $1\text{H}_2\text{O}$. The *methyl* ester crystallises from water in lustrous leaflets and melts at 201—202° (corr.); the *ethyl* ester forms groups of needles and melts at 148—149° (corr.). The *amide* crystallises from hot water in long, slender needles and melts at 280—281° (corr.). The *dianilide* forms long, radiating needles and melts at 227—228° (corr.). *Dehydromucic diacetic anhydride*, $C_{10}H_8O_7$, obtained by the action of acetic anhydride on the acid, crystallises in colourless leaflets; it decomposes at about 150° with liberation of acetic anhydride and formation of *dehydromucic anhydride* as a crystalline sublimate; this substance is probably formed from 2 mols. of the acid, and is therefore represented by the formula $C_{12}H_4O_8$. When the acid chloride is heated with bromine, substitution does not take place. By the action of bromine on potassium dehydromucate, dibromofurfuran tetrabromide is obtained, and by the action of iodine, *diiodofurfuran* is formed, which crystallises in colourless plates and melts at 47°. If bromine is added to an alkaline solution of ethyl dehydromucate, δ -bromopyromucic acid is produced; the corresponding iodopyromucic acid could not be obtained in this manner.

2 : 5-*Dibenzoylfurfuran*, obtained by heating a solution of dehydromucyl chloride in benzene with aluminium chloride, crystallises from

alcohol or light petroleum in lustrous needles, melts at 107° (corr.), sublimes at a higher temperature, and is readily soluble in benzene, chloroform, or glacial acetic acid; when it is heated with bromine water at 140° in a sealed tube, dibromomaleic and *o*-, *m*-, and *p*-bromobenzoic acids are produced. When 2:5-dibenzoylfurfuran is boiled with nitric acid of sp. gr. 1.4, a substance, $C_{18}H_{11}O_5N$, melting at 130 — 131° is produced, together with *o*-, *m*-, and *p*-nitrobenzoic acids, and a small quantity of a crystalline substance which melts at 194 — 195° . 2:5-Dibenzoylfurfuran *diphenylhydrazone* crystallises in needles and melts at 155 — 156° (corr.). The *dioxime* is obtained in two modifications, both of which are readily soluble in acetone or ethyl acetate; the α -*dioxime* crystallises in long, slender needles, and when heated melts at 213 — 214° and is partially converted into the β -form; the β -modification forms groups of minute, irregular plates and melts at 243 — 245° .
E. G.

Reduction of Dehydromucic Acid. By HENRY B. HILL and ALVIN S. WHEELER (*Amer. Chem. J.*, 1901, 25, 463—485. Compare preceding abstracts).—The two isomeric acids obtained by Seelig by the reduction of dehydromucic acid with sodium amalgam, were separated by him by means of their barium salts. After the removal of these salts, the authors have obtained the salt of a third or γ -acid from the mother liquor; they have also found that these acids may be more readily separated by means of their lead salts.

α -Dihydrofurfuran-2:5-dicarboxylic acid is almost exclusively obtained if the reduction is carried on at 0° and a rapid stream of carbon dioxide is passed into the solution; it is readily soluble in water, alcohol, or ether, crystallises in plates or needles, and melts at 149 — 150° (corr.). The solubility of the barium salt in water at 18° is 0.2 per cent.; the calcium salt crystallises with $1\frac{1}{2}H_2O$; the *lead* salt, with $1H_2O$, is soluble in water to the extent of 0.046 at 20° , and 1.03 per cent. at 99.5° . When the acid is heated at 190° in a current of hydrogen, carbon monoxide is evolved, and a sublimate is obtained consisting of the original acid together with a small quantity of slender needles melting at 130° , which are probably pyromucic acid. On oxidation with nitric acid or alkaline potassium permanganate, the acid is converted into dehydromucic and oxalic acids. If the acid is heated with bromine in a sealed tube at 140° , hydrogen bromide and dehydromucic acid are produced, whilst by the action of bromine on an aqueous solution at the ordinary temperature, a *dibromide*,



is obtained which crystallises in prisms containing $1H_2O$, melts at 112 — 113° , and is readily soluble in alcohol or ether; when left over sulphuric acid, it becomes anhydrous and melts at 147 — 148° (corr.). By the action of sodium amalgam or zinc dust on the dibromide, the α -acid is regenerated; when its aqueous solution is treated with barium hydroxide and left for 24 hours, barium pyromucate, bromide, and carbonate are produced. If an aqueous solution of the α -acid is saturated with chlorine, α -chlorohydroxytetrahydrofurfuran-2:5-dicarboxylic acid, $C_6H_7O_6Cl$, is formed, which crystallises in prisms, decomposes at

209—210° (corr.), dissolves readily in water, alcohol, or acetone, and when treated with acetic anhydride yields a well crystallised product.

β -Dihydrofurfuran-2:5-dicarboxylic acid, which may be obtained by boiling a solution of the α -acid with sodium hydroxide, or directly from dehydromucic acid by modifying slightly the method of reduction, crystallises in needles, melts at 178—179° (corr.), and is readily soluble in alcohol. The solubility of the barium salt in water is 1.40 per cent. at 20°; the calcium salt crystallises with $2\frac{1}{2}\text{H}_2\text{O}$; the lead salt with $1\text{H}_2\text{O}$, is soluble in water to the extent of 0.0013 per cent. at 20°, and 0.022—0.032 per cent. at 99.5°. When the β -acid is oxidised with nitric acid, dehydromucic and oxalic acids are formed, whilst by the action of alkaline potassium permanganate, oxalic acid only is produced. The dibromide dissolves readily in alcohol or ether, decomposes at 213—214° (corr.), and is readily reduced to the β -acid by means of sodium amalgam; when an aqueous solution of this compound is treated with barium hydroxide, barium pyromucate, bromide, and carbonate are produced. By the action of chlorine on the β -acid, the compound $\text{C}_6\text{H}_7\text{O}_6\text{Cl}, 1\frac{1}{2}\text{H}_2\text{O}$ is obtained, which crystallises in truncated prisms, melts at 95°, and reacts with acetic anhydride to form a crystalline product.

γ -Dihydrofurfuran-2:5-dicarboxylic acid, obtained by boiling the β -acid for a long time with sodium hydroxide solution, crystallises in stellate groups of plates, decomposes at 190—200° according to the rate of heating, and dissolves readily in alcohol or hot glacial acetic acid. Whilst the α - and β -acids are not affected by sodium amalgam, the γ -acid is converted into the two isomeric tetrahydrofurfuran-2:5-carboxylic acids recently described by Lean (Trans., 1900, 77, 103). The γ -acid is readily oxidised by nitric acid or alkaline potassium permanganate with formation of dehydromucic and oxalic acids. The dibromide, $\begin{array}{c} \text{CH}_2-\text{CH}(\text{CO}_2\text{H}) \\ \text{CHBr}\cdot\text{CBr}(\text{CO}_2\text{H}) \end{array} > \text{O}$, crystallises in prisms, decomposes at about 200°, and dissolves in water or alcohol to form unstable solutions; by the action of barium hydroxide on this compound, pyromucic acid is not produced. E. G.

Insoluble Coumarone- and Indene-Resins. By GUSTAV KRAEMER and ADOLF SPILKER (Ber., 1901, 34, 1887—1889. Compare Störmer, Abstr., 1900, i, 650).—The analyses previously given (Abstr., 1900, i, 656) were obtained from a soluble resin, and fresh analyses of insoluble coumarone-resins prove that combined sulphur is always present (8.5—9.94 per cent.). When subjected to destructive distillation, it yields sulphur, sulphur dioxide, hydrogen sulphide, and practically the same products as were obtained from the soluble resin. The resin obtained from indene (*loc. cit.*) was in reality derived from coumarone and methylcoumarone contained in the indene.

J. J. S.

Conversion of Coumalic Acid into an Isomeride of Dehydromucic Acid. By FRANZ FEIST (Ber., 1901, 34, 1992—1996).—Furfuran-2:4-dicarboxylic acid, $\text{CH} \begin{array}{c} \text{C}(\text{CO}_2\text{K})\cdot\text{CH} \\ \text{C}(\text{CO}_2\text{K})\cdot\text{O} \end{array} + \text{H}_2\text{O}$, prepared

by the action of aqueous potassium hydroxide on methylbromocoumalate, crystallises from water in glistening flakes, melts at 266° , and sublimes slowly below the melting point. The *calcium*, *barium*, and *silver* salts are described. The acid decolorises permanganate and bromine water, but does not reduce ammoniacal silver solutions, and does not lose carbon dioxide when heated alone at 270° , or with acetic acid at 170° . The *methyl* ester crystallises from methyl alcohol in glistening prisms and melts at $109-110^{\circ}$. T. M. L.

3'-Hydroxyflavone. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1901, **34**, 1690—1693).—*m-Ethoxyacetophenone*, prepared by ethylating the corresponding phenol, is a colourless oil which boils at 255° , and readily condenses with ethyl *o*-methoxybenzoate in presence of sodium to form *ω-o-methoxybenzoyl-3-ethoxyacetophenone*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$, which crystallises from dilute alcohol in white needles and melts at 63° ; when the latter is added to warm hydriodic acid, it loses alcohol (1 mol.), and yields *3'-ethoxyflavone*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} - \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt} \\ \parallel \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$, which forms white needles, melts at 118° , and, when boiled for several hours with the concentrated acid, loses its ethoxyl group, giving *3'-hydroxyflavone*. This crystallises from dilute alcohol in broad, white prisms, melts at 208° , and yields a sparingly soluble, crystalline *sodium* salt; the *acetyl* derivative forms white needles or prisms and melts at 97° . W. A. D.

Syntheses in the Chromone Group. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1901, **34**, 1693—1698. Compare Bloch and von Kostanecki, *Abstr.*, 1900, i, 308, 502, and Crivelli and von Kostanecki, *ibid.*, i, 668).—[With W. ORTH].—*ω-Propionyl-2:5-diethoxyacetophenone*, $\text{C}_6\text{H}_5(\text{OEt})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COEt}$, obtained by the sodium ethoxide condensation of quinacetophenone diethyl ether with ethyl propionate, crystallises from dilute alcohol in colourless leaflets and melts at 49° ; when heated for 2 hours with hydriodic acid of sp. gr. 1.96, alcohol (1 mol.) is eliminated, and *6-hydroxy-2-ethylchromone*, $\text{OH} \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} - \text{CEt} \\ \parallel \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$, formed. It separates from alcohol in

long, spear-shaped crystals, melts at 165° , and gives a solution in concentrated sulphuric acid which shows a greenish-blue fluorescence. The *acetyl* derivative forms white leaflets and melts at $92-93^{\circ}$; the *methyl* ether crystallises from alcohol in rhombic plates melting at $87-88^{\circ}$, and the *ethyl* ether from light petroleum in prisms melting at $65-66^{\circ}$. Both of the ethers show a greenish-blue fluorescence in concentrated sulphuric acid solution. When the ethyl ether is heated with alcoholic sodium ethoxide for several hours at 100° , it is resolved into quinacetophenone monoethyl ether and propionic acid.

[With L. PAUL].—*ω-Propionyl-2:4-diethoxyacetophenone*, obtained by condensing ethyl propionate and resacetophenone diethyl ether, crystallises from dilute alcohol in prisms, melts at $74-75^{\circ}$, and with hydriodic acid yields initially *7-ethoxy-2-ethylchromone*, and finally *7-hydroxy-2-ethylchromone*; the former crystallises from dilute alcohol in sheaves of needles (+ $1\text{H}_2\text{O}$) melting at $83-84^{\circ}$, the latter in short

prisms melting at 186° . 7-Acetoxy-2-ethylchromone forms white prisms and melts at $67-68^{\circ}$. All these compounds show a violet-blue fluorescence when dissolved in concentrated sulphuric acid.

[With W. WINTER.]—*ω*-Butyryl-2:4-diethoxyacetophenone, from ethyl butyrate and resacetophenone diethyl ether, forms thick, white needles and melts at $60-61^{\circ}$. 7-Hydroxy-2-propylchromone crystallises from alcohol in thick, colourless needles and melts at 148° ; the *acetyl* derivative forms white leaflets and melts at $64-65^{\circ}$. W. A. D.

Derivatives of 1:4-Benzopyranol, the Parent Substance of a new class of Colouring Matters. II. By CARL BÜLOW and HERMANN WAGNER (*Ber.*, 1901, 34, 1782—1804. Compare this vol., i, 400).—Resorcinol condenses with benzoylacetone in presence of hydrogen chloride to form 7-hydroxy-2-phenylanhydro-4-methyl-1:4-benzopyranol,

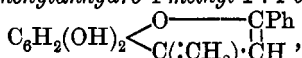
$\text{OH} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{O} \text{---} \text{CPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{CH}_2) \quad \text{CH} \end{array}$; the hydrochloride, $\text{C}_{18}\text{H}_{12}\text{O}_2 \cdot \text{HCl} \cdot \text{H}_2\text{O}$, crystal-

lises from dilute alcohol containing a little free hydrogen chloride in yellow needles or in brownish-yellow tablets, which are less readily soluble than the needle-shaped modification; it becomes red at about 140° , and blackens at 280° . The *anhydro-base*, $\text{C}_{18}\text{H}_{12}\text{O}_2$, is a dark-red, amorphous powder, and chars, without melting, when heated. The substance is hydrolysed by a 10 per cent. solution of potassium hydroxide to acetophenone and resacetophenone. The *picrate* of the anhydro-base separates in yellow prisms when picric acid is added to a solution of the hydrochloride in a mixture of alcohol and acetic acid. The *acetyl* derivative, $\text{C}_{18}\text{H}_{14}\text{O}_3$, exists in two modifications; when prepared in the cold by the action of acetic anhydride on an alkaline solution of the base, it is obtained as a white, amorphous powder, which sinters at $155-160^{\circ}$ but has no definite melting point, dissolves readily in most organic solvents, and is converted by heating with acetic anhydride and sodium acetate into the coloured modification; this is best prepared by heating the base with acetic anhydride and sodium acetate, sinters above 300° , is insoluble in most organic solvents, but dissolves in hot aniline, pyridine, or nitrobenzene, and crystallises from the latter in brown flakes with a dark green, metallic lustre. The *methyl ether*, $\text{C}_{17}\text{H}_{14}\text{O}_3$, also exists in two modifications; the amorphous form, prepared by the action of methyl sulphate on an alkaline solution of the base, is obtained as a white, flocculent precipitate, is readily soluble in most solvents, and sinters at $120-125^{\circ}$; the crystalline modification, prepared by the action of methyl iodide and sodium methoxide, sinters at $261-263^{\circ}$, is only slightly soluble in most solvents, but dissolves in aniline, nitrobenzene, and pyridine, and crystallises from a mixture of pyridine and methyl alcohol in brownish-red needles with a dark green, metallic lustre.

7-Hydroxy-2-phenyl-4-methylbenzopyran, $\text{OH} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{O} \text{---} \text{CPh} \\ \diagup \quad \diagdown \\ \text{CHMe} \quad \text{CH} \end{array}$, pre-

pared by reducing the colour base with zinc dust and hydrogen chloride, is a yellowish-white powder which readily oxidises in the air when moist, dissolves easily in organic solvents, and sinters at $155-160^{\circ}$; the *acetyl* derivative, $\text{C}_{18}\text{H}_{16}\text{O}_3$, is a white, amorphous powder, dissolves in most solvents, does not oxidise in the air, and sinters at $115-120^{\circ}$.

5 : 7-Dihydroxy-2-phenylanthydro-4-methyl-1 : 4-benzopyranol,



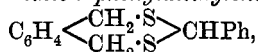
is prepared by condensing phloroglucinol with benzoylacetone; the *hydrochloride*, $\text{C}_{16}\text{H}_{12}\text{O}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$, crystallises in stout, orange-red needles, is insoluble in most organic solvents, and blackens between 200° and 250° ; the *anhydro-base*, $\text{C}_{16}\text{H}_{12}\text{O}_3$, is a reddish-brown, amorphous powder, readily soluble in most solvents, and blackens when heated above 100° ; when hydrolysed with aqueous potassium hydroxide, it gives acetophenone and phloracetophenone. The *picrate* crystallises from dilute alcohol in glistening, orange-red needles. The *acetyl* derivative was obtained as a brownish-white, amorphous powder.

The *hydrochloride* of 7 : 8-dihydroxy-2-phenylanthydro-4-methyl-1 : 4-benzopyranol, $\text{C}_6\text{H}_2(\text{OH})_2 \begin{array}{c} \text{O} \text{---} \text{CPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{:CH}_2) \cdot \text{CH} \end{array} \cdot \text{HCl}$, prepared by condensing pyrogallol with benzoylacetone, crystallises in minute, reddish-brown, rhombic tablets, and chars when heated above 200° ; the *base*, $\text{C}_{16}\text{H}_{12}\text{O}_3$, is a black, crystalline powder, which dissolves to a violet solution in most organic solvents; boiling with aqueous potassium hydroxide hydrolyses it to acetophenone and gallacetophenone. The *picrate*, $\text{C}_{22}\text{H}_{10}\text{O}_{10}\text{N}_3$, forms dark violet, hexagonal tablets. The *diacetyl* derivative, $\text{C}_{20}\text{H}_{16}\text{O}_5$, prepared by the action of sodium acetate and acetic anhydride on the base, resembles the crystalline monoacetoxy-compound; it is insoluble in most solvents, but crystallises from nitrobenzene in reddish-brown, transparent flakes with a dark green, metallic lustre.

T. M. L.

Ring Compounds containing Sulphur. By WILHELM AUTENRIETH and R. HENNINGS (*Ber.*, 1901, 34, 1772—1778).—*o*-Xylylene mercaptan, $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{SH})_2$, condenses with acetone in presence of hydrogen chloride to cyclo-*o*-xylylene-1 : 3-dithio-2-dimethylmethylene, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{S} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{S} \end{array} \text{CMe}_2$, which crystallises from alcohol in glistening flakes, and is not reduced to the mercaptan by zinc and dilute hydrogen chloride. The *disulphone*, $\text{C}_{11}\text{H}_{14}\text{S}_2\text{O}_4$, is a white, crystalline powder which melts above 300° , and is insoluble in water and most organic solvents, but soluble in nitric and sulphuric acids.

cyclo-*o*-Xylylene-1 : 3-dithio-2-phenylmethylene,



crystallises from alcohol in minute, white needles, melts at 170° , and is not reduced to the mercaptan by zinc and dilute hydrogen chloride. The *disulphone*, $\text{C}_{15}\text{H}_{14}\text{O}_4\text{S}_2$, melts above 300° , is insoluble in most solvents, but crystallises from a mixture of acetone and water in glistening, white prisms and minute needles, and dissolves unchanged in sulphuric acid. The *bromo-derivative*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{SO}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{SO}_2 \end{array} \text{CPhBr}$, crystallises from acetone in glistening flakes and melts and decomposes at 268° .

T. M. L.

Conversion of Dextrorotatory Arginine into its Optically Inactive Isomeride. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1901, **32**, 476—478).—*L*-Arginine is readily produced by the tryptic fermentation of fibrin. *D*-Arginine may be obtained by heating *D*-arginine with concentrated sulphuric acid to incipient boiling, or by dehydrating *D*-arginine nitrate at 80°, and then heating at 210—220° for 15—20 mins. J. J. S.

Oxidation Products of Arginine. II. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1901, **32**, 413—418. Compare this vol., i, 403).—The products obtained by the oxidation of arginine are γ -guanidinebutyric acid, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$, and the oxidation products of this, namely, guanidine and succinic acid. γ Guanidinebutyric acid forms a hydrochloride, $\text{C}_5\text{H}_{11}\text{O}_2\text{N}_3\cdot\text{HCl}$, melting at 184° (uncorr.), and readily soluble in water. These results confirm Schulze and Winterstein's (Abstr., 1898, i, 281; 1899, i, 107; 1900, i, 110) and Ellinger's (*ibid.*, 1900, i, 143) conclusions regarding the constitution of arginine.

J. J. S.

1-Methyl-2-vinylpiperidine. By MARTIN HEIDRICH (*Ber.*, 1901, **34**, 1889—1893).—1-Methyl-2-vinylpiperidine, which was prepared in small quantity by Ladenburg (Abstr., 1893, i, 426), has been obtained on a larger scale by heating 1-methylpipecolylalkine (1-methyl-2-hydroxyethylpiperidine) with concentrated hydrochloric acid in sealed tubes at 165—175°. It is a colourless oil with a strong odour resembling that of coniine, boils at 60° under 12 mm. pressure, and is readily volatile in a current of steam; it dissolves slightly in water, more readily in alcohol or ether, and when kept for some time, or when distilled at the ordinary pressure, it polymerises. Its *platini-chloride*, $(\text{C}_8\text{H}_{15}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$, forms bushy masses of small, shining, reddish needles or pyramidal crystals which dissolve readily in hot water and melt at 188°. The *aurichloride* separates from water in small, deformed crystals melting at 115—120°.

Reduction of 1-methyl-2-vinylpiperidine with tin and hydrochloric acid yields 1-methyl-2-ethylpiperidine (see Ladenburg, Abstr., 1898, i, 339), which gives a *mercurichloride*, $\text{C}_8\text{H}_{17}\text{N}\cdot\text{HCl}\cdot 6\text{HgCl}_2$, melting at 201—206°, and a *picrate* melting at 175—176°.

1-Methyl-2-pipecolylalkine iodide hydriodide [1-methyl-2-iodoethylpiperidine hydriodide], $\text{C}_5\text{NH}_9\text{Me}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{I}\cdot\text{HI}$, prepared by the action of phosphorus and hydriodic acid, melts at 163° when deposited from benzene, and at 155—158° when obtained from alcohol by the addition of ether; it forms pale yellow needles readily soluble in water, alcohol, chloroform, or benzene. When repeatedly shaken with freshly precipitated silver hydroxide (2 mols.), the hydriodide (1 mol.) yields mainly 1-methyl-2-hydroxyethylpiperidine with a small quantity of 1-methyl-2-vinylpiperidine.

T. H. P.

Synthesis of Ecgonic Acid. By RICHARD WILLSTÄTTER and CHARLES HOLLANDER (*Ber.*, 1901, **34**, 1818—1819).— Δ^8 -Hydro-muconic acid combines with hydrogen bromide to form β -bromoadipic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises in prisms melting at 147°. When heated with a solution of methylamine in benzene, this acid gives an almost quantitative yield of ecgonic acid,

$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}\left\langle\begin{array}{c}\text{NMe}\cdot\text{CO} \\ \text{CH}_2-\text{CH}_2\end{array}\right.$; the synthetic (racemic) acid melts at 93—94°, and agrees in its properties and salts with the acid obtained from tropine. The *copper* salt is very soluble in water and is precipitated by acetone in emerald-green prisms.

This synthesis affords the first direct proof of the presence of the pyrrolidine ring in tropine and ecgonine. A. H.

Action of Cuminaldehyde on α -Picoline (2-Methylpyridine). By P. BACKE (*Ber.*, 1901, **34**, 1893—1896).—When cuminaldehyde and α -picoline are heated together in a sealed tube, the following two products are obtained.

(1.) 2-Hydroxy- β -p-isopropylphenylethylpyridine,
 $\text{C}_5\text{NH}_4\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\text{Pr}^\beta$,

which is formed when the two compounds are heated at 140° in presence of water, crystallises from alcohol in white needles having a satiny lustre and melting at 80°; it is readily soluble in alcohol, ether, acetone, or benzene. The *platinichloride*, melting at 201°, the *aurichloride* (with $1\text{H}_2\text{O}$), melting at 107—108°, the *picrate*, melting at 135°, and the *ferrocyanide* were analysed.

(2.) isoPropyl- α -stilbazole, $\text{C}_5\text{NH}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Pr}^\beta$, is obtained when cuminaldehyde and picoline are heated at 240—250° in a sealed tube; it separates from ether as a white, crystalline mass melting at 47°, and dissolves readily in ether or alcohol but only slightly in acids. Its *mercurichloride*, melting at 143°, *platinichloride* (with $2\text{H}_2\text{O}$), melting at 170°, and its *picrate*, melting at 189—190°, were prepared. It gives a *dibromide*, $\text{C}_{16}\text{H}_{17}\text{NBr}_2$, separating from alcohol in snow-white, sparkling leaflets melting at 159—160°. On reduction with sodium and alcohol, the base yields isopropyl- α -stilbazoline, $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Pr}^\beta$, which is a colourless oil boiling at 300—305° under the ordinary pressure, at 176° under 16 mm., and at 110° under 10 mm. pressure; on exposure to air, it turns yellowish, and when kept cold it slowly deposits very deliquescent, white needles; in presence of water, the base has a strongly alkaline reaction towards litmus paper. Its *hydrochloride*, melting at 150°, *hydrobromide*, melting at 148°, and *platinichloride* (with $4\text{H}_2\text{O}$), melting at 85°, were analysed. T. H. P.

***o*-Nitrophenyl-5-ethyl-2-picolyalkine [5- β -Hydroxy- β -*o*-nitrophenylethyl-1-ethylpyridine] and its Derivatives.** By W. CASTNER (*Ber.*, 1901, **34**, 1897—1901).—5- β -Hydroxy- β -*o*-nitrophenylethyl-2-ethylpyridine, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_3\text{Et}$, prepared by heating molecular proportions of *o*-nitrobenzaldehyde and aldehyde-collidine with water in a sealed tube at 150°, separates from dilute alcohol in silky, white needles which melt at 110° and dissolve readily in alcohol or acetone and to a less extent in ether; its *aurichloride*, melting at 138°, *platinichloride*, melting at 161°, and *mercurichloride* were analysed. Reduction of the base with mild reducing agents gives a small yield of the corresponding amino-compound, $\text{C}_{15}\text{H}_{15}\text{ON}_2$, which crystallises from dilute alcohol in small, yellow needles melting at 76° and dissolving in alcohol, ether, or acetone; its *hydrochloride* melts at 85°, its *aurichloride* at 117°, and its *platinichloride* at 134°.

When the nitro-compound is reduced with sodium and alcohol, both the pyridine nucleus and the nitro-group undergo reduction, giving rise to a base, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_3\text{Et}$, which is obtained as a yellow oil; the *platinichloride* melting and decomposing at 126° , the *mercurichloride*, and the *aurichloride* were analysed.

5- β -Hydroxy- β -phenylethyl-2-ethylpyridine, $\text{OH} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_3\text{Et}$, prepared by the interaction of benzaldehyde and aldehyde-collidine in presence of water in a sealed tube at 150° , separates from water in white, well-formed crystals melting at 88° , and is readily soluble in alcohol or acetone and to a less extent in ether; the *aurichloride*, melting at 111° , and *platinichloride* were analysed. T. H. P.

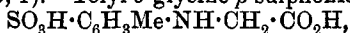
Constitution of the Bases formed by the Action of Alkyl Iodides on the Indoles. By GIUSEPPE PLANCHER (*Gazzetta*, 1901, 31, i, 280—284).—A reply to Brunner's claim of priority in this matter (see this vol., i, 407). T. H. P.

Acyl Derivatives of Indoxyl and of Indoxylic Acid. By DANIEL VORLANDER and B. DRESCHER (*Ber.*, 1901, 34, 1854—1860).—[With F. TELLER].—*Methyl acetylindoxylate* melts at 143 — 144° , the corresponding *ethyl* ester at 136° . *Methyl benzoylindoxylate* crystallises in flat needles melting at 160° and the *ethyl* ester at 163° . The *phenyl cyanate* derivative of ethyl indoxylate melts at 187 — 189° , and is gradually decomposed when boiled with alcohol. *Methyl diacetylindoxylate*, $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{N} \text{Ac} \\ \text{C}(\text{OAc}) \end{smallmatrix} \right\rangle \text{C} \cdot \text{CO}_2\text{Me}$, obtained by the action of acetic anhydride and sodium acetate, crystallises in plates melting at 83 — 84° , and the *ethyl* ester in needles melting at 82° . Acyl derivatives of indoxylic acid may readily be obtained by shaking alkaline solutions of the acid with acid anhydrides or chlorides; the acyl compounds thus obtained are identical with those formed by acylating the dry acid in the absence of alkali. *Acetylindoxylic acid* melts and decomposes at 175° , and gives a dark colour with ferric chloride. *Propionylindoxylic acid*, $\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}$, melts at 163° , and *benzoylindoxylic acid* at 196° .

1-*Acetylindoxyl*, $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{N} \text{Ac} \\ \text{C}(\text{OH}) \end{smallmatrix} \right\rangle \text{CH}$, obtained when indoxyl is left in contact with acetic anhydride for half an hour, crystallises from hot water in flat needles, melts at 136° , gives no colour with ferric chloride, and is soluble in alkalis. When its dilute potassium hydroxide solution is shaken with acetic anhydride, diacetylindoxyl melting at 82° is formed. 3-*Acetylindoxyl*, obtained by the action of acetic anhydride on alkaline solutions of indoxyl, crystallises in plates, melts at 126° , and its alcoholic solution gives no coloration with ferric chloride, but an acetic acid solution develops a dark violet-red colour with a little concentrated nitric acid or bromine water; it is not so readily further acetylated as the 1-compound. 1-*Nitroso-3-acetylindoxyl* crystallises in pale yellow needles, melts at 83° , and is insoluble in cold alkalis.

3:3'-*Dipropionyl-indigo-white*, $\text{C}_{22}\text{H}_{20}\text{O}_4\text{N}_2$, melts and partially decomposes at 218° ; the *dibenzoyl* compound decomposes at about 240° , and on oxidation yields brownish-red crystals of dibenzoylindigo, which decompose above 200° . J. J. S.

Constitution of Indigo-carmine. By DANIEL VORLÄNDER and PHILIPP SCHUBART (*Ber.*, 1901, 34, 1860—1863. Compare Schlieper, *Annalen*, 1861, 120, 1).—Tolyl-*o*-glycine-*p*-sulphonic acid,

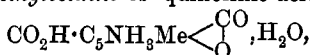


obtained by the oxidation of *o*-aminotoluene-*p*-sulphonic acid (*Annalen*, 1869, 155, 8) with alkali chlorates, yields a *monosodium* salt, $\text{C}_9\text{H}_{10}\text{O}_5\text{NSNa}\cdot 5\text{H}_2\text{O}$, and a *potassium* salt, $\text{C}_9\text{H}_{10}\text{O}_5\text{NSK}\cdot \text{H}_2\text{O}$. When oxidised in alkaline solution with permanganate, it yields 4-sulphophenyl-2-glycine-1-carboxylic acid, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, the *monopotassium* salt of which contains $2\text{H}_2\text{O}$. The dehydrated salt after condensation with acetic anhydride and sodium acetate, and treatment with dilute alkali, yields an isomeride of indigo-carmin.

Indigo-carmin itself may be obtained by similar methods from 6-aminotoluene-*m*-sulphonic acid (Neville and Winther, *Trans.*, 1880, 37, 625), and must therefore contain the sulphonic acid groups in ortho-positions to the carbonyl groups.

The *monosodium* salt of 5-sulphophenylglycine-1-carboxylic acid contains $4\text{H}_2\text{O}$, but the *potassium* salt is anhydrous. J. J. S.

Betaine of Quinolinic Acid. By ALFRED KIRPAL (*Monatsh.*, 1901, 22, 361—374).—The methylbetaine of quinolinic acid is not obtained when the acid is heated with methyl alcohol and methyl iodide. Quinolinic anhydride and methyl iodide combine when heated at 100° to form an additive methiodide, $\text{C}_8\text{NH}_4\text{MeI} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$; the latter, when dissolved in hot water and treated with silver oxide, becomes converted into the *methylbetaine* of quinolinic acid,



which crystallises in large, monoclinic plates [$a : b : c = 0.556 : 1 : 2.019$, $\beta = 105^\circ.2$] melting and decomposing at 151° . It is a strong monobasic acid which rapidly decomposes when suspended in boiling alcohol into carbon dioxide and trigonelline.

The *calcium* salt, $(\text{C}_8\text{H}_6\text{O}_4\text{N})_2\text{Ca}\cdot 3\text{H}_2\text{O}$, and the *silver* salt, with H_2O , both form short prisms. The *methyl* ester of the betaine, $\text{CO}_2\text{Me}\cdot\text{C}_5\text{NH}_3\text{Me} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$, prepared from the methiodide of quinolinic

anhydride and methyl alcohol, or from the α -methyl ester of quinolinic acid and methyl iodide, or by the action of methyl iodide on the silver salt of the betaine, crystallises in four- or six-sided plates melting and decomposing at 163° . The *ethyl* ester forms large, lustrous leaflets melting and decomposing at 160° . The *amide*, prepared by the action of ammonia on the methyl ester, crystallises in yellowish, quadratic plates or pyramids with H_2O , which becomes coloured at 200° and decomposes at 230° .

The author concludes that in the betaine, anhydride formation has taken place between the nitrogen and the 3-carboxyl group, as the methyl ester can be obtained from the α -methyl ester of quinolinic acid.

The *methochloride* of quinolinic acid, $\text{C}_8\text{NH}_3\text{MeCl}(\text{CO}_2\text{H})_2$, prepared by the action of hot concentrated hydrochloric acid on the betaine, crystallises in prismatic needles decomposing at 220° , and is converted

by heating with alcoholic hydrochloric acid into the methochloride of nicotinic acid.

With thionyl chloride, the betaine reacts vigorously, producing the methochloride of quinolinic anhydride. K. J. P. O.

Oxidation of Indigo-white with Oxygen. By WILHELM MANCHOT and JOHANNES HERZOG (*Annalen*, 1901, 316, 318—330. Compare Abstr., 1900, i, 30, and this vol., ii, 93).—When an alkaline solution of indigo-white, obtained from pure synthetical indigo by reduction with zinc dust and sodium hydroxide, is shaken with air, the primary oxidation takes place in accordance with the equation $C_{16}H_{12}O_2N_2 + O_2 = C_{16}H_{10}O_2N_2 + H_2O_2$. The hydrogen peroxide combines with alkali present forming the corresponding peroxide, and if this happens to be soluble, the following secondary action occurs, $C_{16}H_{12}O_2N_2 + H_2O_2 = C_{16}H_{10}O_2N_2 + 2H_2O$. This loss of peroxide occurs in the presence of the alkali hydroxides, ammonia, and even borax; when barium hydroxide is employed, the secondary change is entirely prevented, and the process then affords a means of estimating the indigo-white in an indigo vat. The amount of peroxide produced is found by treating the mixture with lead peroxide and sulphuric acid, the volume of oxygen evolved being a measure of the indigo-white present. Lead peroxide is employed in preference to alkali permanganate and ferricyanide because these reagents oxidise the indigo, yielding gaseous products. The results obtained are tabulated, and the paper contains a sketch of an apparatus suitable for this estimation. G. T. M.

Isomeric Hydrazones. By EUGEN BAMBERGER and OTTO SCHMIDT (*Ber.*, 1901, 34, 2001—2017).— α -Nitroformaldehydephenylhydrazone, $NO_2 \cdot CH:N_2HPh$ (Abstr., 1900, i, 566), melts sharply at $74.5-75.5^\circ$ when heated from 70° , but when heated from 20° undergoes partial isomeric change, and does not liquefy completely at 75° ; when reheated after being fused and allowed to solidify, it melts sharply at $84.5-85.5^\circ$, and consists entirely of the β -phenylhydrazone. The α -isomeride is only partially altered by benzene, chloroform, light petroleum, or ether, but is completely changed into the β -isomeride by absolute or dilute alcohol; the β -isomeride, on the other hand, is unaltered by alcohol, but is converted partially by benzene, and completely by chloroform or light petroleum, into the α -isomeride. Neither isomeride has any marked conductivity.

Phenylnitroformaldehydephenylhydrazone, $NO_2 \cdot CPh:N_2HPh$ (Holle-mann, Abstr., 1895, i, 455), is only known in one form melting at $101.5-102.5^\circ$.

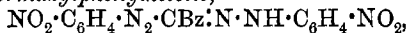
β -Benzoylformaldehydephenylhydrazone, $CHBz:N_2HPh$, prepared from diazobenzene and benzoylacetic acid (Abstr., 1886, 62), crystallises from alcohol in golden-yellow flakes with a bronze-like lustre, and melts, according to the rate of heating, between 136° and 140° ; it has a normal molecular weight in boiling alcohol, and is converted into the α -isomeride, partially when boiled with benzene, and completely when boiled with light petroleum. α -Benzoylformaldehydephenylhydrazone crystallises in rosettes of orange-coloured prisms or in hemimorphic crystals with a violet lustre, melts between

114° and 117°, has a normal molecular weight in boiling benzene solution, and is converted into the β -isomeride to a slight extent when boiled with benzene, but completely when boiled with alcohol or acetone. The α -hydrazine dissolves more readily in benzene or light petroleum than the isomeride, but there is no marked difference in the solubility of the two forms in acetone or alcohol. When heated above the melting point, both isomerides are converted into a mixture melting between 126° and 128°. A specimen of the α -isomeride was found after five years to have passed completely at the ordinary temperature into the β -isomeride. Benzoylformaldehydephenylhydrazine is a feeble acid; the sodium salt forms small red needles, and is decomposed by atmospheric carbon dioxide and by water; acids usually convert it into a mixture of the α - and β -isomerides, but in one case the β -isomeride was alone produced.

β -Benzoylformaldehyde-o-nitrophenylhydrazine,
 $\text{CHBz} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$,

prepared from *o*-nitrophenyldiazonium acetate and potassium benzoylacetate, crystallises from a mixture of alcohol and acetone in glistening, golden needles, melts at 145·5—146·5° when heated from 100°, but at 141·5—142·5° when heated from 20°, and has a normal molecular weight in freezing benzene. When a solution of the β -hydrazine in acetic acid, acetone, or benzene is allowed to evaporate, the residue consists partly of needles of the α -hydrazine melting between 113° and 117°, but on recrystallisation the β -hydrazine is reproduced. The α -hydrazine dissolves more readily than the β -hydrazine in acetone or benzene, or in warm alkaline hydroxides. When heated above the melting point, the α -hydrazine is converted very largely into the β -hydrazine, and remelts at 139—140°, and a specimen which had been kept at atmospheric temperature during $3\frac{1}{2}$ years also melted at 137—138°, and only sintered very slightly at 114°. A mixture of isomerides was obtained by dissolving in alcoholic sodium ethoxide and pouring into ice-cold hydrochloric acid.

Di-m-dinitroformazylphenylketone,

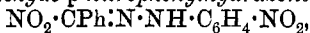


which is formed as a by-product in the action of *m*-nitrophenyldiazonium acetate on potassium benzoylacetate, separates from xylene in dark red crystals and melts and decomposes at 210°. α -Benzoylformaldehyde-*m*-nitrophenylhydrazine crystallises from light petroleum or benzene in orange-yellow, metallic needles with a violet lustre, and melts at 139—140°; prolonged boiling with alcohol converts it into the β -modification, which crystallises in orange-brown needles with a blue-violet lustre and melts between 149° and 152°, or into a γ -modification which separates in dull, whitish-yellow nodules; boiling with light petroleum and benzene converts the β - (or γ -) modification into the α -, and a similar change takes place when the substance is fused; the β -modification does not appear to be soluble in benzene except by conversion into the α -modification.

Benzoylformaldehyde-p-nitrophenylhydrazine crystallises from xylene in glistening, sulphur-yellow flakes with a violet lustre, melts at 199—200°, and is not known in more than one modification.

T. M. L.

Benzaldehydephenylhydrazone. By EUGEN BAMBERGER and JAC. GROB (*Ber.*, 1901, **34**, 2017—2023).—When benzaldehydephenylhydrazone suspended in glacial acetic acid is acted on at low temperatures by nitrous fumes, it is converted into phenylnitroformaldehydephenylhydrazone, $\text{NO}_2 \cdot \text{CPh} \cdot \text{N} \cdot \text{NHPh}$, identical with the substance obtained by V. Meyer from diazobenzene and phenylnitromethane (compare *Abstr.*, 1899, i, 108, and von Pechmann, *Abstr.*, 1893, i, 461). At the same time, nitration takes place in the benzene-ring, and a smaller amount of *phenylnitroformaldehyde-p-nitrophenylhydrazone*,



is produced; this was also prepared from sodium isophenylnitromethane and *p*-nitrodiazobenzene nitrate; it crystallises from alcohol in minute, felted, silky, dark orange-red needles, and melts at 140.5° when heated from 135° . Phenyldiazonium and *p*-nitrophenyldiazonium nitrates are also found amongst the by-products of the action; they are probably produced by hydrolysis of the preceding compounds to benzaldehyde and the hydrazines, and the subsequent action of nitrous acid on the latter.

T. M. L.

1:2:4-Substituted Iminazoles. By FRANZ KUNCKELL and P. DONATH (*Ber.*, 1901, **34**, 1829—1833. Compare *Abstr.*, this vol., i, 293).—2:4-Diphenyliminazole readily forms an *ethiodide*,

$\text{CH} \begin{smallmatrix} \text{NH} \cdot \text{CPh} \\ \diagup \quad \diagdown \\ \text{CPh} \cdot \text{N} \cdot \text{EtI} \end{smallmatrix}$, which crystallises in small, white needles melting

at 162° . Silver oxide converts this into 2:4-diphenyl-1-ethyliminazole, $\text{C}_{17}\text{H}_{16}\text{N}_2$, which is also formed by the action of ethyl iodide on silver diphenyliminazole, and crystallises in white needles melting at 194° . This compound again forms an *ethiodide*, $\text{C}_{19}\text{H}_{21}\text{N}_2\text{I}$, which melts at 154° . The corresponding *chloroacetic ester* derivative melts at 260° , and the *bromoacetic ester* compound at 236° .

2:4-Diphenyliminazole phenacyl bromide, $\text{CH} \begin{smallmatrix} \text{NH} \cdot \text{CPh} \\ \diagup \quad \diagdown \\ \text{CPh} \cdot \text{N} \cdot \text{Br}(\text{CH}_2\text{Bz}) \end{smallmatrix}$,

readily formed from diphenyliminazole and phenacyl bromide, crystallises in white needles melting at 222° . On treatment with aqueous soda, hydrogen bromide is eliminated with the production of 2:4-diphenyl-1-phenacyliminazole, $\text{C}_{23}\text{H}_{18}\text{ON}_2$, which crystallises in plates melting at 142 — 143° . This substance readily forms an *ethiodide*,

$\text{CH} \begin{smallmatrix} \text{N}(\text{CH}_2\text{Bz}) \cdot \text{CPh} \\ \diagup \quad \diagdown \\ \text{CPh} \text{---} \text{N} \cdot \text{EtI} \end{smallmatrix}$, which melts at 202° . It has, however, been

found impossible to obtain an additive compound with phenacyl bromide, diphenyliminazole phenacyl bromide being invariably produced.

Bromine converts diphenylphenacyliminazole into a *monobromo*-compound, which melts at 176° , and is not decomposed by dilute aqueous soda. It probably contains the bromine atom in the methylene group of the phenacyl residue, but this has not yet been definitely ascertained.

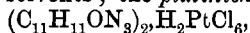
A. H.

I. Pyrimidines and Cyanidines from Paranitrobenzamidine.

II. Attempt to prepare *o*-Nitrobenziminio-ether. By THEODOR RAPPEPORT (*Ber.*, 1901, **34**, 1983—1992).—6-Hydroxy-2-*p*-nitrophenyl-

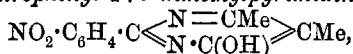
4-methylpyrimidine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{N} \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{CH}$, prepared by the action of sodium hydroxide on a mixture of ethyl acetoacetate and *p*-nitrobenzamidine hydrochloride, crystallises from acetic acid in minute needles, melts at 296° , is only sparingly soluble in most solvents, but dissolves readily in alkalis or acids, or in pyridine; the silver salt, $\text{C}_{11}\text{H}_8\text{O}_3\text{N}_3\text{Ag}$, forms a white precipitate.

6-Hydroxy-2-*p*-aminophenyl-4-methylpyrimidine, $\text{C}_{11}\text{H}_{11}\text{ON}_3$, prepared by reducing the nitro-compound with tin and hydrogen chloride, crystallises from dilute alcohol in microscopic, colourless prisms, melts at 233° , and dissolves in acids, alkalis, alcohol, or pyridine, but only sparingly in most other solvents; the platinichloride,



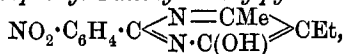
crystallises in yellow prisms and decomposes at 250° ; the silver salt forms a white precipitate.

6-Hydroxy-2-*p*-nitrophenyl-4 : 5-dimethylpyrimidine,



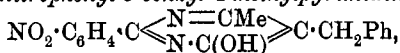
prepared from ethyl methylacetoacetate, crystallises from acetic acid in minute, colourless needles, does not melt at 305° , dissolves readily in acids or alkalis, but is only slightly soluble in most solvents. The amino-compound, $\text{C}_{12}\text{H}_{13}\text{ON}_3$, prepared by reducing the preceding compound, crystallises from dilute alcohol in yellowish, glistening flakes, melts and decomposes at 287° , and is readily soluble in alcohol; its platinichloride, $(\text{C}_{12}\text{H}_{13}\text{ON}_3)_2 \cdot \text{H}_2\text{PtCl}_6$, forms glistening, yellow prisms.

6-Hydroxy-2-*p*-nitrophenyl-4-methyl-5-ethylpyrimidine,



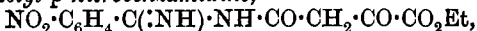
prepared from ethyl ethylacetoacetate, crystallises from dilute acetic acid in long, yellowish, silky needles, dissolves readily in acids and alkalis, and melts and decomposes at 292° . The amino-compound, $\text{C}_{13}\text{H}_{15}\text{ON}_3$, prepared by reduction, crystallises from dilute alcohol in small, brownish prisms, is readily soluble in alcohol and in acids or alkalis, and melts and decomposes at 246° ; its platinichloride, $(\text{C}_{13}\text{H}_{15}\text{ON}_3)_2 \cdot \text{H}_2\text{PtCl}_6$, forms microscopic, yellow, glistening prisms, and decomposes above 275° .

6-Hydroxy-2-*p*-nitrophenyl-5-benzyl-4-methylpyrimidine,



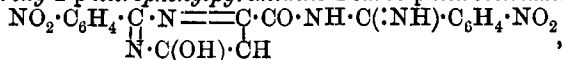
prepared from ethyl benzylacetoacetate, crystallises from dilute acetic acid in long, slender, yellowish needles, melts at 264° , and dissolves readily in acids or alkalis, or in alcohol.

Ethoxalylacetyl-*p*-nitrobenzamidine,

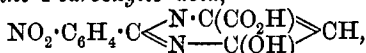


prepared by the action of ethyl oxalylacetate on *p*-nitrobenzamidine, forms small, brown prisms, melts and decomposes at 205° , dissolves readily in acids and alkalis and in pyridine, but is only sparingly soluble in most solvents.

6-Hydroxy-2-*p*-nitrophenylpyrimidine-4-carbo-*p*-nitrobenzamidine,



is also produced in this reaction, and is separated from the preceding compound by extracting with water, from which it separates as an oil, and is not readily obtained in crystals. 6-Hydroxy-2-*p*-nitrophenylpyrimidine-4-carboxylic acid,



prepared by the action of sodium hydroxide on the mixed product from ethyl oxalylacetate and *p*-nitrobenzamidine, separates from acetic acid in minute crystals, melts and decomposes between 261° and 262°, dissolves readily in alcohol or in alkalis, but not in dilute acids; the *basic barium* salt, $\text{C}_{11}\text{H}_5\text{O}_5\text{N}_3\text{Ba}$, is a crystalline precipitate, and when washed with dilute acetic acid is converted into the normal *barium* salt, $(\text{C}_{11}\text{H}_6\text{O}_5\text{N}_3)_2\text{Ba}$. A third substance, produced by the interaction of *p*-nitrobenzamidine and ethyl oxalylacetate, is a *compound*, $\text{C}_{28}\text{H}_{81}\text{O}_{12}\text{N}_3$, of 1 mol. of the amidine with 2 mols. of the ester, which crystallises from benzene in small prisms, and melts and decomposes at 128°; it is at once decomposed by alkalis.

Acetyl-p-nitrobenzamide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NHAc}$, prepared by the action of acetic anhydride on *p*-nitrobenzamidine, forms flat needles, dissolves readily in alcohol and in sodium hydroxide, but only sparingly in acids, and melts at 221°.

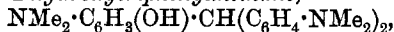
Bis-p-nitrophenylmethylecyanidine, $\text{CMe} \begin{array}{l} \nearrow \text{N} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \\ \searrow \text{N} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \end{array} \gg \text{N}$, also produced in the preceding interaction, forms flat, yellow needles, is very sparingly soluble in water or alcohol, but readily so in chloroform or acetic acid, and melts at 280°.

Di-p-nitrobenzamidinecarbamide, $\text{CO}[\text{NH} \cdot \text{C}(\text{:NH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2]_2$, prepared by the action of carbonyl chloride on *p*-nitrobenzamidine, forms flat, yellow, four-sided plates, melts and decomposes at 284°, losing ammonia and forming the hydroxycyanidine. *Bis-p-nitrophenylhydroxycyanidine*, $\text{OH} \cdot \text{C} \begin{array}{l} \nearrow \text{N} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \\ \searrow \text{N} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \end{array} \gg \text{N}$, which is also formed directly from carbonyl chloride and *p*-nitrobenzamidine, forms yellow needles, does not melt at 305°, is insoluble in most solvents, but dissolves readily in pyridine or in sodium hydroxide; concentrated sodium hydroxide precipitates the crystalline *sodium* salt.

(An attempt to prepare *o*-nitrobenzimidino-ether from *o*-nitrobenzonitrile, alcohol, and hydrogen chloride gave only a negative result.)

T. M. L.

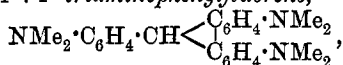
Synthesis of a Phenylldiphenylenemethane Colouring Matter. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1901, 132, 1527—1531).—Hexamethyl-4:4':4'':2-tetraminotriphenylmethane, when diazotised in dilute hydrochloric or sulphuric acid solution, exchanges its amino-group for hydroxyl, yielding *hexamethyl-4:4':4'':2-triamino-2-hydroxytriphenylmethane*,



crystallising from alcohol in needles and melting at 173°. The hydroxy-base is insoluble in aqueous potassium hydroxide solution, but readily dissolves in an alcoholic solution of the alkali; when oxidised with chloranil, it yields a violet colouring matter.

2-Chlorohexamethyl-4 : 4' : 4''-triaminotriphenylmethane, produced when the nitrite is added to a solution of the tetramine in concentrated hydrochloric acid, crystallises in colourless needles and melts at 97°; it is sparingly soluble in hot alcohol, but readily dissolves in benzene or chloroform; when oxidised with manganese dioxide and acetic acid, it yields a crystalline, blue colouring matter, dyeing wool in a neutral bath.

Hexamethyl-4 : 4' : 4''-triaminophenylfluorene,



is obtained when the tetramine is diazotised in 50 per cent. sulphuric acid, the yield, however, not exceeding 35 per cent.; it crystallises from alcohol or benzene in colourless needles and melts at 214°. This compound cannot be obtained by the dehydrating action of sulphuric acid on the hydroxytriamine.

A blue colouring matter is produced when the preceding base is oxidised with lead peroxide; its *hydrochloride*, $\text{C}_{25}\text{H}_{28}\text{N}_3\text{Cl} \cdot 2\frac{1}{2}\text{H}_2\text{O}$, crystallises readily in needles or leaflets somewhat soluble in cold water, but completely precipitated by sodium chloride. When the colouring matter is compared with the crystal violet obtained from the original leuco-base, it is found that the introduction into the molecule of a fluorenic linking results in a change of shade from violet to blue, but produces no other striking modification in the tinctorial properties. The new colouring matter is equally sensitive to acids and alkalis, but less acted on by light; the affinity for animal fibres decreases, whilst that for vegetable fibres increases; it does not exhibit fluorescence.

G. T. M.

Monosubstituted Derivatives of 1 : 3 : 4-Triazole. By GUIDO PELLIZZARI and MATTEO BRUZZO (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 414—420. Compare this vol., i, 488).—The following 1 : 3 : 4-triazole derivatives have been obtained by methods analogous to that described for the preparation of the 1-phenyl compound (*loc. cit.*).

1-p-Tolyl-1 : 3 : 4-triazole, $\text{C}_7\text{H}_7 \cdot \text{N} < \begin{matrix} \text{CH:N} \\ \text{CH:N} \end{matrix}$, crystallises from water

in white leaflets containing $1\frac{1}{2}\text{H}_2\text{O}$ and melting at 83°; the water is given off in a desiccator, the anhydrous form thus obtained melting at 116°. It is extremely soluble in alcohol or chloroform, less so in benzene or ether, and slightly in water or light petroleum; mineral acids readily dissolve it, forming salts from which it is precipitated by potassium hydroxide. Its *platinichloride* forms orange laminæ decomposing at about 215—220°, and on boiling in aqueous solution yields the compound $(\text{C}_7\text{H}_5\text{N}_3)_2\text{PtCl}_4$ as an insoluble, yellow, amorphous powder. The *picrate* crystallises from alcohol in slender, silky, yellow needles melting at 172°.

1-o-Tolyl-1 : 3 : 4-triazole, $\text{C}_9\text{H}_9\text{N}_3$, is deposited from water in prisms melting at 104°, and is very soluble in alcohol or chloroform, moderately so in water or benzene, and to a slight extent in ether. Its *platinichloride* is unstable, and decomposes even in the cold and in presence of hydrochloric acid, yielding the compound $(\text{C}_9\text{H}_7\text{N}_3)_2\text{PtCl}_4$,

in the form of an insoluble, yellow powder. The *picrate* crystallises from dilute alcohol in slender needles melting at 174° .

1- α -Naphthyl-1 : 3 : 4-triazole, $C_{12}H_9N_3$, is deposited from benzene in white crystals melting at 120° and is very soluble in chloroform or alcohol, and to a less extent in ether, light petroleum, or water. The platinichloride could not be obtained as it splits up into the compound, $(C_{12}H_9N_3)_2PtCl_4$, which is an insoluble, yellow powder. The *picrate* separates from alcohol in small crystals melting at 164° .

1- β -Naphthyl-1 : 3 : 4-triazole, is deposited from benzene in minute crystals melting at 160° and is soluble in benzene or chloroform, and slightly so in ether or water. The compound $(C_{12}H_9N_3)_2PtCl_4$ forms an amorphous, yellow powder and the *picrate* of the base separates from alcohol in very small needles melting at 205° . T. H. P.

Trisubstituted Derivatives of 1 : 3 : 4-Triazole. By GUIDO PELLIZZARI and ANTONIO ALCIATORE (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 444—452).—Trisubstituted derivatives of 1 : 3 : 4-triazole may be obtained by methods similar to those employed in the preparation of the 1-phenyl compound (this vol., i, 488), using in place of the formyl derivatives of hydrazine and of the primary amine higher acyl derivatives.

In the preparation of 1-phenyl-2 : 5-dimethyl-1 : 3 : 4-triazole, $NPh \begin{smallmatrix} CMe:N \\ CMe:N \end{smallmatrix}$, the best yield is obtained by the action of diacetylhydrazine on acetanilide; it crystallises from benzene in silky, white needles melting at 237° , which dissolve readily in alcohol, chloroform, or water, and to a slight extent in ether or light petroleum; it is soluble in mineral acids, from which it is precipitated by potassium hydroxide solution, and volatilises when heated. The *platinichloride* separates from hydrochloric acid in tufts of needles which melt and decompose at 256 — 257° . The *picrate* is deposited from water or alcohol in long, yellow crystals melting at 175° .

1-o-Tolyl-2 : 5-dimethyl-1 : 3 : 4-triazole, $C_{11}H_{13}N_3$, separates from benzene in white crystals which melt at 168° and dissolve readily in water, alcohol, or chloroform, and to a less extent in ether or light petroleum. Its *platinichloride* crystallises from hydrochloric acid in tufts of needles melting and decomposing at 244 — 245° and when boiled in dilute aqueous solution yields the compound $(C_{11}H_{13}N_3)_2PtCl_4$ as a pale-yellow, amorphous, insoluble powder decomposing at about 255° . The *picrate* separates from alcohol in acicular crystals melting at 164° .

1-p-Tolyl-2 : 5-dimethyl-1 : 3 : 4-triazole crystallises from benzene in minute needles melting at 228° and dissolves readily in water, alcohol, or chloroform, and slightly in light petroleum. Its *platinichloride* could not be obtained crystalline, but on boiling with water yields the compound $(C_{11}H_{13}N_3)_2PtCl_4$ as a yellow, insoluble powder melting and decomposing at 250 — 254° . The *picrate* separates from alcohol in slender, yellow crystals melting at 158° .

1 : 2 : 5-Triphenyl-1 : 3 : 4-triazole, $C_{20}H_{15}N_3$, prepared by the interaction either of dibenzoylhydrazine and benzanilide or of dibenzoylhydrazine and aniline, crystallises from alcohol in slender, white

needles melting at 304—305° and dissolves slightly in benzene but is insoluble in water, ether, or light petroleum; it has weak basic properties and forms a *hydrochloride* separating in white crystals.

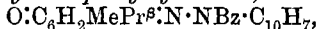
T. H. P.

Constitution of the Hydroxyazo-compounds. By WILLIAM MCPHERSON and HERBERT C. GORE (*Amer. Chem. J.*, 1901, 25, 485—496. Compare Abstr., 1900, i, 123).—*α-Benzoyl-β-acetyl-α-naphthylhydrazine*, obtained by the action of benzoyl chloride on *β*-acetyl-naphthylhydrazine, separates from alcohol in large crystals and melts at 184°; it is converted by dilute sulphuric acid into *α-benzoyl-α-naphthylhydrazine*, $C_{10}H_7 \cdot NBz \cdot NH_2$, which crystallises from alcohol in truncated pyramids, melts at 120·5°, and dissolves readily in alcohol or benzene. On the addition of light petroleum to a benzene solution of the last-mentioned compound, feathery crystals melting at 98° are deposited, but when these are gently heated the melting point gradually rises to 120·5°. The following hydrazones were prepared by the interaction of quinones with *α-benzoyl-α-naphthylhydrazine*.

Quinonebenzoyl-α-naphthylhydrazone, $O:C_6H_4:N \cdot NBz \cdot C_{10}H_7$, crystallises from light petroleum in plates, melts at 113·5°, and is very soluble in benzene, alcohol, ether, or chloroform; both this substance and the isomeric benzoyl-*α-naphthaleneazophenol* yield *α-naphthaleneazophenol* on hydrolysis. *α-Naphthaleneazophenol* may be readily prepared by the action of phenol on *α-naphthyl diazonium chloride*; it melts at 136°, crystallises from alcohol in brown needles, from benzene in yellow needles, and from light petroleum in brown plates which, when heated to 130°, suddenly become red; this red modification separates from a solution in light petroleum in reddish, silky needles. The *benzoate*, $OBz \cdot C_6H_4 \cdot N:N \cdot C_{10}H_7$, crystallises in needles, melts at 120°, and dissolves readily in chloroform or benzene.

Toluquinonebenzoyl-α-naphthylhydrazone, $O:C_6H_3Me:N \cdot NBz \cdot C_{10}H_7$, forms prismatic crystals and melts at 166°; this compound, like the isomeric benzoyl-*α-naphthaleneazo-o-cresol*, yields *α-naphthaleneazo-o-cresol* on hydrolysis. *α-Naphthaleneazo-o-cresol* may be obtained by the interaction of *α-naphthyl diazonium chloride* and *o-cresol*; it crystallises from benzene in reddish-yellow needles, melts at 154·5°, and is readily soluble in alcohol or benzene. Its *benzoate* crystallises from light petroleum in long, thin, flat needles and melts at 120°.

Thymoquinonebenzoyl-α-naphthylhydrazone,



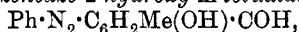
crystallises from alcohol in rhombohedra, melts at 151·5°, and furnishes *α-naphthaleneazothymol* on hydrolysis. *α-Naphthaleneazothymol*, prepared by the action of thymol on *α-naphthyl diazonium chloride*, separates from a mixture of benzene and light petroleum in monoclinic crystals, melts at 117·5°, and is soluble in ether, benzene, or alcohol. Its *benzoate* crystallises in needles, dissolves readily in ether or benzene, and melts at 173·5°.

E. G.

Hydroxyazoaldehydes. By WALTHER BORSCHKE and C. E. BOLSER (*Ber.*, 1901, 34, 2094—2104. Compare Abstr., 1900, i, 419).—*p*-Hydroxybenzaldehyde does not react with a diazo-solution prepared from aniline, whilst *m*-hydroxybenzaldehyde undergoes a vigorous

reaction accompanied by evolution of nitrogen, but does not yield a colouring matter. The semicarbazones of the isomeric hydroxybenzaldehydes have not previously been described. The *meta*-compound crystallises in compact, yellow needles melting at 198°; the *para*-compound is a yellowish, crystalline powder melting at 223—225°, and the *ortho*-compound crystallises in faintly yellow needles melting at 231—232°. Resorcyaldehyde, $C_6H_3(OH)_2 \cdot CHO$ [2:4:1], readily reacts with diazobenzene chloride, but the product is very unstable in alkaline solution. *Benzeneazoresorcyaldehyde* is therefore best prepared in alcoholic solution, but can only be recrystallised in small quantities. The *phenylhydrazone*, $Ph \cdot N_2 \cdot C_6H_2(OH)_2 \cdot CH:N \cdot NHPh$, crystallises in lustrous, blackish-brown needles which melt and decompose at 217°.

o-Cresolaldehyde (2-hydroxy-*m*-tolualdehyde) reacts with diazobenzene chloride to form 5-benzeneazo-2-hydroxy-*m*-tolualdehyde,



which crystallises in yellowish-red needles melting at 76°. The same compound can be prepared from benzeneazo-*o*-cresol by Tiemann and Reimer's reaction. The *anilide* crystallises in brownish-yellow plates melting at 77—78°; the *phenylhydrazone* forms yellowish-red plates melting at 147—148°; and the *α -naphthylimine* crystallises in large plates which have a golden lustre and melt at 158—160°. A diazo-solution prepared from sulphanilic acid also reacts with this aldehyde, forming sodium 5-*p*-sulphobenzeneazo-2-hydroxy-*m*-tolualdehyde, $SO_3Na \cdot C_6H_4 \cdot N_2 \cdot C_6H_2Me(OH) \cdot CHO, 2H_2O$, which crystallises in yellowish plates. On treatment with bromine, it yields 5-bromo-2-hydroxy-*m*-tolualdehyde, $OH \cdot C_6H_2BrMe \cdot CHO$, which is also formed by the direct action of bromine on *o*-hydroxytolualdehyde, and crystallises in silky needles melting at 78°. The *phenylhydrazone* crystallises in yellowish plates and melts at 137—138°. 5-Bromo-2-hydroxy-*m*-toluic acid, $OH \cdot C_6H_2BrMe \cdot CO_2H$, is formed by the direct bromination of 2-hydroxy-*m*-toluic acid, and crystallises in white needles melting at 231—232°; the *barium* salt is moderately soluble in water. 2-Hydroxy-1-methyl-3-ketophenylpropenyl-5-benzeneazobenzene, $Ph \cdot N_2 \cdot C_6H_2Me(OH) \cdot CH:CH \cdot C(=O)Ph$, is formed by the condensation of benzeneazohydroxytolualdehyde with acetophenone, and forms a reddish-yellow, crystalline powder which melts and decomposes at 180—181°. The corresponding sodium sulphonate is prepared in a similar manner from sulphobenzeneazohydroxytolualdehyde, and forms reddish-yellow crystals. All attempts to obtain the corresponding saturated compounds have hitherto proved unavailing. 3-Hydroxy-*p*-tolualdehyde readily reacts with diazobenzene chloride to form 6-benzeneazo-3-hydroxy-*p*-tolualdehyde, which melts at 143—144°. The *phenylhydrazone* crystallises in lustrous plates melting at 123—125°. 6-Hydroxy-*m*-tolualdehyde and 4-hydroxy-*m*-tolualdehyde do not react with diazobenzene chloride.

A. H.

Benzylazide [Benzylazoimide]. By THEODOR CURTIUS and AUGUST DARAPSEY (*J. pr. Chem.*, 1901, ii, 63, 428—444. Compare Abstr., 1900, i, 698, 699).—Benzylazoimide can be obtained, not only from nitrosobenzylhydrazine (*loc. cit.*), but also by the interaction of silver-

azoimide and benzyl iodide. The stability towards alkalis cannot therefore be accounted for by supposing that benzylazoimide has not the constitution of an ester of azoimide. By the action of mineral acids (sulphuric and hydrochloric), the azoimide undergoes a series of decompositions, which are thus represented by the authors :

(1) $\text{CH}_2\text{Ph}\cdot\text{N}_3 = \text{CH}_2\text{Ph}\cdot\text{N} < + \text{N}_2$. The group $\text{CH}_2\text{Ph}\cdot\text{N} <$ is then partly transformed either into $\text{CHPh}\cdot\text{NH}$, an iminoaldehyde which with water gives benzaldehyde and ammonia ; or (2) into CH_2NPh , a methyleneamine, which then with water yields aniline and formaldehyde. (3) The azoimide partly also reacts with water, forming benzylamine and nitrous oxide ; $\text{CH}_2\text{Ph}\cdot\text{N}_3 + \text{H}_2\text{O} = \text{CH}_2\text{Ph}\cdot\text{NH}_2 + \text{N}_2\text{O}$. (4) Lastly, azoimide is evolved probably owing to hydrolysis of benzylazoimide. The authors point out that the formation of aniline virtually represents the replacement of CH_3 by NH_2 .

In carrying out the experiments, benzaldehyde was separated by distilling in steam from the acid product of the reaction. After making alkaline, the ammonia, aniline, and benzylamine are distilled over in steam, and the last two separated by passing carbon dioxide into their ethereal solution, when benzylamine carbonate is precipitated. When the acid liquor is neutralised, a yellow base is precipitated which is insoluble in all solvents except chloroform ; it decomposes at 250° , and is readily soluble in acids, forming a red solution ; its diazo-derivative condenses with resorcinol, yielding a red azocolouring matter. This base is also obtained by the action of sulphuric acid on a mixture of aniline and paraformaldehyde, and on anhydroformaldehydeaniline. Hydrochloric acid differs from sulphuric acid in its action on benzylazoimide in producing less benzaldehyde, and more benzylamine and yellow base.

Details are given in the paper of the preparation of the azoimide from benzylhydrazine, the *dihydrochloride* of which crystallises in short thick prisms melting at 145° with evolution of gas. Boiling with water, alcohol, or alcoholic potash are without effect on benzylazoimide, and it is not oxidised by prolonged boiling with aqueous lead nitrate.

K. J. P. O.

Auto-oxidation of Hydrazobenzene. By WILHELM MANCHOT and JOHANNES HERZOG (*Annalen*, 1901, **316**, 331—332. Compare this vol., i, 565 ; ii, 93).—When hydrazobenzene, dissolved in an alcoholic solution of sodium ethoxide, is shaken with oxygen, the amount of this gas absorbed corresponds with the equation $\text{N}_2\text{H}_2\text{Ph}_2 + \text{O}_2 = \text{H}_2\text{O}_2 + \text{N}_2\text{Ph}_2$. The hydrogen peroxide produced interacts with the sodium ethoxide yielding sodium peroxide, which, under these conditions, is precipitated ; in this way, any secondary change due to the oxidising action of the peroxide on the organic compound is entirely prevented.

G. T. M.

Hydrazo-compounds. Reduction Products of *o*- and *p*-Nitrodiphenyl and the Products of the Transformation of Hydrazodiphenyls. By GEORG FRIEBEL and BERTHOLD RASSOW (*J. pr. Chem.*, 1901, [ii], **63**, 444—465).—The compound described by Zimmermann (*Abstr.*, 1881, 175) as *p*-hydrazodiphenyl is shown to be slightly impure *p*-azodiphenyl (m. p. 249°). *p*-Hydrazodiphenyl, $\text{N}_2\text{H}_2(\text{C}_6\text{H}_4\text{Ph})_2$,

is prepared by the reduction of *p*-nitrodiphenyl by alcoholic potassium hydroxide and zinc dust, and is purified by recrystallisation from ether, every precaution being taken to avoid contact with the air, which immediately oxidises it to the azo-compound; the base forms colourless leaflets melting at 167—169°. By concentrated hydrochloric acid it is converted into *p*-aminodiphenyl (m. p. 53°). The *hydrochloride* of the latter forms leaflets, the *sulphate* needles, and the *platinichloride* golden-yellow leaflets (compare Hübner, *Annalen*, 1881, 209, 342). The *diacetyl* derivative crystallises in white needles melting at 120°. The *benzoyl* derivative of *p*-hydroxydiphenyl crystallises in colourless needles melting at 147—148°.

o-Azoxydiphenyl, prepared by reduction of *o*-nitrodiphenyl, forms crystals melting at 157—158°.

o-Hydrazodiphenyl, prepared by reduction of the last-mentioned compound, crystallises in colourless needles melting at 182°, which are only slowly oxidised by the air.

3:3'-Diphenylbenzidine is formed on heating the hydrazo-compound at 100° with concentrated hydrochloric acid, and crystallises in large plates melting at 151—152°. The *dihydrochloride* crystallises in needles, little soluble in water, and the *platinichloride* in yellow leaflets. The *diacetate*, formed when the base is boiled with acetic anhydride, melts at 224—227°; the *diacetyl* derivative, prepared by heating the base at 100° with thioacetic acid, crystallises in colourless needles melting at 245—246°. With carbon disulphide, the base gives an insoluble, crystalline compound melting at 195—196°.

o-Azodiphenyl, prepared by oxidising *o*-hydrazodiphenyl with ferric chloride, crystallises in reddish-purple needles melting at 144.5°.

K. J. P. O.

Products of the Digestion of Albumin. III. The so called **Amphopeptone**. By SIGMUND FRÄNKEL and LEO LANGSTEIN (*Monatsh.*, 1901, 22, 335—345. Compare *Abstr.*, 1899, i, 396).—Recent work has shown that Kühne's amphopeptone is a mixture of two very different substances. The authors find that on treatment with alcohol amphopeptone partly dissolves. The soluble fraction yields only the biuret reaction, gives a precipitate with bromine or iodine in potassium iodide, and contains sulphur. On benzoylating by Schotten-Baumann's method and extracting with ether, a soluble benzoyl derivative of a compound free from sulphur goes into solution, whilst a small quantity of an insoluble substance containing sulphur remains. The soluble benzoyl compound gives only the biuret reaction, and is probably the derivative of a protamine.

The fraction insoluble in alcohol consists of two parts, a peptone which gives Millon's, the biuret, and the xanthoproteic reactions, and a substance which gives Molisch's reaction, and is identical with the carbohydrate complex of albumin (albamin).

In the experiments, coagulated albumin, prepared from egg-albumin free from globulin, was digested with pure pepsin in the presence of hydrochloric acid. The peptone was isolated in some cases by saturating the fluid products of digestion with ammonium sulphate at 100°, filtering, and adding twice the volume of alcohol; the alcoholic

extract was evaporated and then poured into absolute alcohol, when the fraction insoluble in this medium separates. Addition of ether precipitates from the alcohol the soluble fraction, which gives only the biuret reaction. In other cases, the fluid products of digestion were evaporated under reduced pressure, and the residual syrup extracted with alcohol; from the solution, ether precipitated the soluble fraction.

From Witte's peptone, a soluble fraction was obtained in a similar manner.

K. J. P. O.

Chemical Nature of Trypsin. By P. A. LEVENE (*Amer. J. Physiol.*, 1901, 5, 298—300).—The experiments recorded do not justify the conclusion that trypsin is a nucleo-compound. Only those solutions are active which give the biuret test; this would seem to indicate that trypsin is of proteid nature. However, in some cases the biuret test was scarcely perceptible, and yet the solution of self-digested trypsin still contained the active ferment.

W. D. H.

Action of Trypsin on Fibrin. By HORACE M. VERNON (*J. Physiol.*, 1901, 26, 405—426).—The method suggested for the estimation of the tryptic value of a pancreatic extract is as follows. About 1.8 c.c. of finely chopped fibrin are introduced into a 10 c.c. graduated tube filled with distilled water. This is centrifugalised for 2 minutes. The volume of fibrin, now reduced to about 1 c.c., is read off. Five c.c. of the water are then replaced by 2 per cent. solution of sodium carbonate, and the mixture kept at 38° for an hour; the fibrin swells up. Six c.c. of liquid are then withdrawn, and replaced by water containing 1 c.c. of the extract to be tested. After a given time, centrifugalisation is again performed for 1 minute, and the volume of the remaining fibrin read off. The time is noted when about 80 per cent. of the fibrin has disappeared; this is corrected to exactly 80 per cent., and so tables of relative tryptic value can be constructed. Each estimation takes about a quarter of an hour. Sodium carbonate rapidly destroys trypsin, and trypsin appears to consist of a series of ferments with different degrees of stability. Allowing for the ferment destroyed during an experiment, the rate of digestion varies as the square root of the quantity of ferment present (Schütz's law).

W. D. H.

Constitution of Organo-mercury Compounds of Benzoic Acid. By LEONE PESCI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 362—363).—The hydroxymercuribenzoic anhydride previously described (see Abstr., 1900, i, 546) by the author is also produced by the action of mercuric acetate on phthalic acid, so that in this anhydride, and also in the corresponding acid and its derivatives, the mercury must occupy the ortho-position to the carboxyl residue, and not the para-position, as was previously supposed (*loc cit.*).

T. H. P.

Organic Chemistry.

Action of Nitric Acid on Secondary Alcohols. By GIACOMO PONZIO (*Gazzetta*, 1901, 31, i, 401—406).—The action of nitric acid on secondary alcohols gives rise to α -diketones as principal product, together with dinitro-paraffins. Methyl ethyl carbinol yields, with nitric acid, dimethyl diketone and dinitroethane; diethyl carbinol gives methyl ethyl diketone and dinitroethane; methyl butyl carbinol, methyl propyl diketone and dinitrobutane, whilst methyl hexyl carbinol and nitric acid yield methyl amyl diketone and dinitrohexane. The statement found in some text-books that the action of nitric acid on diethyl carbinol or on diethyl ketone yields dinitropropane is inaccurate, as the author's results show.

T. H. P.

Preparation of Dimethyl Sulphate. By M. BENNETT BLACKLER (*Chem. News*, 1901, 83, 303—304).—The preparation of dimethyl sulphate from methyl alcohol and sulphuric acid is best carried out in two stages. Dimethyl ether is first prepared and is absorbed in sulphuric acid kept at 160°. This solution, when distilled above 160°, gives a 21 per cent. yield of dimethyl sulphate.

R. H. P.

Ethylene Derivatives. By LOUIS HENRY (*Rec. trav. Chim.*, 1901, 20, 243—254).—Ethylene diacetate readily absorbs hydrogen bromide, yielding acetic acid and bromoethyl acetate, $\text{CH}_3\text{Br} \cdot \text{CH}_2 \cdot \text{OAc}$ (Demole, this Journ., 1874, 783). The latter boils at 162—163°, has a sp. gr. 1.524 at 9°, and solidifies to colourless needles melting at -13.8° . The bromine is readily replaceable, but not quite so readily as in the isomeric ethyl bromoacetate.

Iodoethyl acetate, $\text{CH}_3\text{I} \cdot \text{CH}_2 \cdot \text{OAc}$, obtained by the action of sodium iodide on the bromo-derivative, is a colourless liquid with a pleasant odour, boils at 110° under 60 mm. pressure, and has a sp. gr. 2.441 at 20°. Ethylene monobromohydrin is formed when the bromo-derivative is boiled with water, ethyl alcohol, or best of all with methyl alcohol.

Attempts to prepare bromoethyl acetate by the action of potassium acetate (1 mol.) and a little acetic acid on ethylene dibromide proved fruitless, the product always formed being the diacetate.

Ethylene iodohydrin is readily obtained by the action of sodium iodide on bromoethyl acetate in the presence of methyl alcohol.

J. J. S.

Mixed Glycerides in Natural Fats. By D. HOLDE and M. STANGE (*Ber.*, 1901, 34, 2402—2408).—The authors have investigated the solid constituents of olive oil, which have previously been regarded as a mixture of triolein, tripalmitin, and tristearin. On cooling an ethereal solution of olive oil to -40 or -45° , the solid glycerides separated as a white, crystalline precipitate, which was freed from liquid oil by repeated recrystallisation from ether at a low temperature, and finally from alcohol and ether at the ordinary temperature.

By this means, 5—10 grams of pure solid glyceride were isolated from 400—700 grams of olive oil. The glyceride crystallises from dilute alcohol in soft needles, melting at 29—31°, and having a sp. gr. 0.9948 in the molten state and a mol. wt. 857—860. Determinations of the saponification number, iodine number, total fatty acid, and proportion of glycerol all lead to the conclusion that the glyceride is an oleodimargarin, $C_3H_5(C_{17}H_{33}O_2)_2 \cdot C_{18}H_{33}O_2$.

The glyceride was hydrolysed by a cold alcoholic solution of lead acetate, and the lead salts of the fatty acids separated by extraction with ether. The proportion of solid to liquid acid was found 2.2:1, instead of 1.9:1, required by the above formula. The solid fatty acid melted at 59—61°, was saturated, had a mol. wt. 265.4, and in other ways resembled margaric acid, whilst the mol. wt., iodine number, &c., of the liquid acid were those of oleic acid.

K. J. P. O.

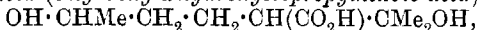
Sorbic Acid. By OSCAR DOEBNER and A. WOLFF (*Ber.*, 1901, 34, 2221—2223. Compare Abstr., 1900, i, 526).—*Sorbyl chloride*, $C_5H_7 \cdot COCl$, prepared by the action of phosphorus pentachloride on the acid, is a colourless liquid which has a penetrating odour, and boils at 78° under 15 mm. pressure. *Methyl sorbate*, $C_5H_7 \cdot CO_2Me$, prepared from the alcohol and sorbyl chloride, is a colourless liquid which boils at 174° and freezes at 5°. Ethyl sorbate is best prepared from the chloride, and has already been described by Hofmann (*Annalen*, 1859, 110, 137). *Sorbamide*, $C_5H_7 \cdot CO \cdot NH_2$, crystallises in slender needles melting at 168°. *Sorbanilide*, $C_5H_7 \cdot CO \cdot NHPh$, crystallises in lustrous scales melting at 153°. *Sorbonitrile*, $C_5H_7 \cdot CN$, is a colourless oil and boils at 72° under 20 mm. pressure. The *ketone*, $C_5H_7 \cdot COEt$, prepared by Freund's reaction with zinc ethyl, is a light yellow coloured oil which boils at 90—95° under 26 mm. pressure.

A. H.

Cineolic Acid. III. By HANS RUPE and MAX RONUS (*Ber.*, 1901, 34, 2191—2206. See Abstr., 1900, i, 371, and this vol., i, 119).—The acid obtained (*loc. cit.*) by the action of sulphuric acid on cineolic acid is stereoisomeric with the cinenic acid previously described (*loc. cit.*); it is now called β -cinenic acid to distinguish it from the latter, which is called α -cinenic acid; this is probably an instance of *cis*- and *trans*-isomerism.

α -Cinenic acid, when treated with hydrogen bromide in glacial acetic acid solution, yields δ -bromo α -hydroxyisopropylhexoic acid, $CHMeBr \cdot CH_2 \cdot CH_2 \cdot CH(CO_2H) \cdot CMe_2 \cdot OH$, which crystallises in stellate needles, melts at 97—98°, and, when treated with alcoholic potash, yields the α -hydroxyisopropyl- γ -hexenoic acid previously described, and, when treated with water, cinogenic acid.

Cinogenic acid (δ -hydroxy- α -hydroxyisopropylhexoic acid),



which forms the portion insoluble in ether of the products of the action of water under pressure on cineolic acid, crystallises in glistening, six-sided tablets, melts at 104.5—105°, and forms easily soluble salts, except the *magnesium* and *cobalt* salts, which both crystallise with $2H_2O$;

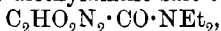
when distilled under reduced pressure, or heated with water under pressure, it yields α -cinenic acid.

β -Cinenic acid is a clear oil boiling at $122-123^\circ$ under 10 mm. pressure, has a conductivity $\lambda_{1024}-\lambda_{32}$ 11.44 at 20° , and a refractive index n_D 1.4486; it forms a characteristic *calcium* salt, which crystallises in stellate needles, and has a solubility of 1 part in 74.4 parts of water at 17° , the corresponding salt of α -cinenic acid being amorphous, and having a solubility of 1 part in 460 parts of water at 17° . α -Cinenic acid can be converted into the β -isomeride by heating with dilute sulphuric acid under pressure, and the latter can also be converted into cinogenic acid by the method described above. R. H. P.

Product of Nitration of Ethyl Acetoacetate. By LOUIS BOUVEAULT and A. BONGERT (*Compt. rend.*, 1901, 133, 103—104).—By the nitration of ethyl acetoacetate, the authors have obtained a substance, $C_2N_2O_2(CO_2Et)_2$, which is an oil, isomeric with the substance obtained by Scholl (this vol., i, 359) by the action of silver nitrate on ethyl bromoacetate, and called by him ethyl bisanhydronitroacetate. The diamide prepared by Scholl melted and exploded at 121° , whilst the isomeric *amide* obtained by the authors melted at 253° . Scholl prepared a number of crystalline diamides from his ester, and both primary and secondary amines; with primary amines, on the other hand, the authors obtained only oily products, whilst with secondary amines a more profound reaction took place.

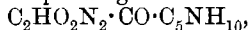
When dimethylamine is passed into an ethereal solution of the ester, heat is developed, and the solution becomes of a bright red colour. A red oil separates and soon solidifies. This substance, $C_7H_{14}O_3N_4$, forms red crystals, melting at 129° , and is the dimethylamine salt of an acid, $C_5H_7O_3N_3$, which separates in crystals melting and decomposing at 182° . From the ethereal mother liquor of the dimethylamine salt, ethyl alcohol and dimethylurethane were obtained. The reaction between the ester and dimethylamine may be thus represented: $3NHMe_2 + C_2O_2N_2(CO_2Et)_2 = C_2H_6O + NMe_2 \cdot CO_2Et + C_5H_7O_3N_3 \cdot NHMe_2$. To the acid, the formula $C_2HO_2N_2 \cdot CO \cdot NMe_2$ is given.

With diethylamine, the diethylamine salt of an acid,



is obtained; the acid forms ruby-red crystals, melting and decomposing at 143° ; the salt, $C_7H_{11}O_3N_3 \cdot NHEt_2$, crystallises in orange scales melting at 112° . The urethane was not isolated.

With piperidine, the ester gave alcohol, piperidylurethane, and the piperidine salt of the corresponding acid. The acid,

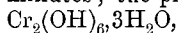


forms orange-red crystals melting and decomposing at 162° ; the piperidine salt, orange crystals melting and decomposing at 148° . Piperidylurethane, $C_6H_{10}N \cdot CO_2Et$, is a colourless liquid boiling at 103° under 20 mm. pressure. K. J. P. O.

Chromium Oxalate. By GRÉGOIRE N. WYROUBOFF (*Chem. Centr.*, 1901, i, 1362—1363; from *Bull. Soc. franç. Min.*, 24, 86—92).—An amorphous chromium oxalate, soluble in water in all proportions, is obtained by reducing chromic acid in presence of oxalic acid, or by

dissolving chromium oxide in oxalic acid. When the solution is evaporated at the ordinary temperature by exposure to the air, it leaves a violet liquid, but when evaporated on the water-bath, a green liquid remains, which, on treatment with water, becomes violet. The normal chromium oxalate, $\text{Cr}_2\text{O}_3 \cdot 3\text{C}_2\text{O}_3 \cdot 25\text{H}_2\text{O}$, forms monoclinic, violet crystals, and is obtained by mixing a solution of an alkali oxalate (3 mols.) with a freshly prepared 10–15 per cent. solution of a chromium salt (1 mol.). From concentrated solutions of chromium salts, an oxalate containing $13\text{H}_2\text{O}$ separates in grey needles, which in the dry state may be kept without change, but forms very unstable solutions. The hydrate containing $25\text{H}_2\text{O}$ loses $12\text{H}_2\text{O}$ on exposure to the air for a long time, or on boiling with alcohol for a few minutes. Both hydrates are completely insoluble in water; the last mol. of water cannot be removed without partial decomposition. The hydrates, with $4\text{H}_2\text{O}$ and $1\text{H}_2\text{O}$ respectively, are crystalline substances soluble in water or alcohol. They are to be regarded as abnormal salts of the composition $\text{Cr}_2\text{O}_2(\text{OH})_2 \cdot \text{C}_3\text{O}_4\text{H}_2$ and $\text{Cr}_2\text{O}_2(\text{OH})_2 \cdot 3\text{C}_2\text{O}_3$ respectively, whilst the normal oxalates contain more water, and have the composition $\text{Cr}_2(\text{OH})_6 \cdot 3\text{C}_2\text{O}_4\text{H}_2 \cdot 19\text{H}_2\text{O}$ and $\text{Cr}_2(\text{OH})_6 \cdot 3\text{C}_2\text{O}_4\text{H}_2 \cdot 7\text{H}_2\text{O}$ respectively.

When a crystalline chromium salt (1 mol.) is treated with cold sodium hydroxide or potassium hydroxide solution (6 mols.), a pale green oxide is formed, which, after drying over sulphuric acid, has the composition $\text{Cr}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ or $\text{Cr}_2(\text{OH})_6 \cdot 5\text{H}_2\text{O}$. It loses $2\text{H}_2\text{O}$ at 110° without alteration of colour, and at a considerably higher temperature forms the hydrate $\text{Cr}_2\text{O}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$; the last mol. of water is given off only at a red heat. The abnormal oxalate does not give a precipitate with cold sodium hydroxide or potassium hydroxide solutions, but only after boiling for some minutes; the precipitated oxide,



loses $2\text{H}_2\text{O}$ at 110° .

E. W. W.

Influence of Molybdic Acid and Molybdates on the Specific Rotation of Malates. By HERRMANN ITZIG (*Ber.*, 1901, 34, 2391–2401. Compare Gernez, *Abstr.*, 1889, 1147; 1890, 744; 1891, 291).—Saturated solutions of normal sodium or potassium *l*-malate readily dissolve molybdic acid. The composition of the dissolved sodium salt (dimolybdylmalate) is represented by the formula $\text{Na}_2\text{O} \cdot 2\text{MoO}_3 \cdot \text{C}_4\text{H}_4\text{O}_4$, and has $[\alpha]_D + 743^\circ$ at 17° , whilst the potassium salt has $[\alpha]_D + 731^\circ$ at 18° . Solutions of molybdylmalates, $\text{M}'_2\text{O} \cdot \text{MoO}_3 \cdot \text{C}_4\text{H}_4\text{O}_4$, are obtained by dissolving molybdic acid (1 mol.) in solutions of malates (1 mol.); the sodium salt has $[\alpha]_D + 136^\circ$ at 17° , and the potassium salt $[\alpha]_D + 153.9^\circ$ at 18° . Molybdylmalates, $(\text{M}'_2\text{O} \cdot \text{H}_2\text{O} \cdot \text{C}_4\text{H}_4\text{O}_4)_2 \cdot \text{MoO}_3$, have been prepared as crystalline compounds by Henderson (*Trans.*, 1899, 75, 542). The ammonium salt has $[\alpha]_D - 87.2^\circ$ at 17° . In the case of all the above salts, $[\alpha]_D$ decreases with dilution.

The author has investigated the action of molybdic acid and sodium molybdate and paramolybdate on the specific rotation of *l* malic acid and its normal and acid sodium and ammonium salts. In all cases, addition of the molybdenum compound initially increases the *l*ævorota-

tion of the malic acid or its salt to a maximum. As the proportion of the former increases, the levorotation begins to decrease, and finally passes into a dextrorotation, which in some cases becomes very great.

K. J. P. O.

Brown-Coal Tar. By THEODOR ROSENTHAL (*Zeit. angew. Chem.*, 1901, 14, 665—667. Compare Abstr., 1892, 1075, and 1895, i, 258).—The following substances have been found in the products of destructive distillation of brown coal:—(a) Saturated and unsaturated aldehydes, the only one isolated in a pure state, so far, is acetaldehyde. (b) Ketones, both acetone and methyl ethyl ketone have been isolated. (c) Methyl alcohol. (d) Acetonitrile.

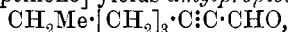
J. J. S.

Action of Acid Chlorides on Methanal [Paraformaldehyde]. By LOUIS HENRY (*Compt. rend.*, 1901, 133, 96—98. Compare Abstr., 1900, i, 537).—Chloromethyl acetate is formed in the reaction of acetyl chloride on paraformaldehyde. When a fragment of fused zinc chloride is present (compare Descudé, this vol., i, 357), the reaction takes place more easily. By a similar method, *chloromethyl benzoate*, $C_6H_5 \cdot CO_2 \cdot CH_2Cl$, is obtained from benzoyl chloride and paraformaldehyde; the ester is an oil which, at 200° , decomposes into its constituents.

K. J. P. O.

Syntheses of Aldehydes of the Acetylene Series. By CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1901, 133, 105—107. Compare this vol., i, 442).—On adding the sodium derivatives (1 mol.) of the acetylene hydrocarbons, suspended in absolute ether at 0° to ethyl formate (2 mols.), an immediate reaction takes place and the liquid becomes yellow. After 6 hours' standing at 0° the major part of the sodium derivative has disappeared. Ice is added, and the ethereal layer separated; after evaporation of the ether, the residue, which consists chiefly of an aldehyde of the acetylene series, is distilled under reduced pressure (yield from 15—18 per cent.).

Cenanthylidene [heptinene] yields *amylpropiolaldehyde*,



a colourless liquid, distilling at 89° under 26 mm. and at 185 — 187° under atmospheric pressure.

Phenylacetylene yields phenylpropiolaldehyde (Claisen, Abstr., 1893, i, 422, 423), which boils at 127 — 128° under 28 mm. pressure, and has a sp. gr. 1.0791 at 0° . The absence of the typical hydrogen atom of the acetylene hydrocarbons prevents the formation of metallic derivatives. With boiling aqueous solutions of alkalis, these aldehydes decompose, yielding the acetylene hydrocarbon and a formate. From amylpropiolaldehyde is also formed some methyl amyl ketone, and traces of hexoic acid.

The authors express the opinion that initially an additive product of the sodium acetylide and ethyl formate is formed; with water, this decomposes partly into an aldehyde, alcohol, and sodium hydroxide, and partly into the original acetylene hydrocarbon, alcohol, and sodium formate.

K. J. P. O.

Action of Hydrogen Sulphide on Acetylacetone. By F. LETEUR (*Compt. rend.*, 1901, 133, 48—49).—Hydrogen sulphide has

no action on acetylacetone, alone or in presence of acetic acid and sodium acetate, but in presence of concentrated hydrochloric acid a polymeric dithioacetylacetone, $(C_5H_8S_2)_2$, is obtained. It is volatile in steam, and forms long channelled, acicular, triclinic prisms which melt at $162-163.5^\circ$, and sublime at a lower temperature. It is soluble in most organic solvents and in hot alcohol, but is only slightly so in cold alcohol and insoluble in water. C. H. B.

Cellulose. By RICHARD WOLFFENSTEIN and G. BUMCKE (*Ber.*, 1901, 34, 2415—2417. Compare Abstr., 1899, i, 852; Tollens, this vol., i, 453).—A controversial paper. W. A. D.

Dextrorotatory sec. Butylamine. By JOHANNES GADAMER (*Arch. Pharm.*, 1901, 239, 283—294. Compare Abstr., 1899, i, 534).—The sec. butylamine, prepared from the dextrorotatory sec. butylthiocarbamide (from *Cochlearia officinalis*) (*loc. cit.*), is now shown to be dextrorotatory and not inactive ($[\alpha]_D + 6.42^\circ$ at 15.5°). A list is given of the specific and molecular rotations of sec. butyl- carbamide, -thiocarbamide, and -thiocarbimide derivatives; and the influence of the different groups attached to the asymmetric carbon atom on the magnitude of the specific rotation is discussed.

sec. Butylamine is prepared from the essential oil of *Cochlearia officinalis* by reduction with zinc dust and sulphuric acid in dilute alcoholic solution; it has a sp. gr. 0.7393. The hydrochloride is very hygroscopic, and in aqueous solution has $[\alpha]_D - 2.05^\circ$ at 20° ; the *platinichloride* forms dark, yellowish-red prisms, melting and decomposing at $204-210^\circ$. sec. Butylthiocarbimide is obtained by the action of carbon disulphide on the amine; addition of mercuric chloride to the product precipitates the mercuric salt of butylthiocarbamic acid, which decomposes at the ordinary temperature into mercuric sulphide and butylthiocarbimide.

d-d-Dibutylcarbamide, prepared by the action of mercuric oxide on d-d-dibutylthiocarbamide, crystallises in needles which have $[\alpha]_D + 39.71^\circ$ at 20° when in solution in absolute alcohol.

K. J. P. O.

Derivatives of Ethylene Ethyl Alcohol and Ethylene Acetic Acid. By LOUIS HENRY [and PAUL DALLE] (*Rec. trav. Chim.*, 1901, 20, 255—258).—*Ethylene ethylamine* [*trimethylenecarbinylumine*], $\begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix} > CH \cdot CH_2 \cdot NH_2$, is obtained when ethyleneacetonitrile (Abstr., 1899, i, 676) is reduced with sodium and absolute alcohol; it is a colourless liquid boiling at 88° and soluble in water; on treatment with nitrous acid, it yields a small amount of *trimethylenecarbinol* (*ethylene ethyl alcohol*), $\begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix} > CH \cdot CH_2 \cdot OH$, boiling at 130° under

756 mm. pressure. *Trimethylenecarboxylic chloride*, $\begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix} > CH \cdot COCl$, boils at $120-122^\circ$ under 754 mm. pressure. A comparison of the boiling points of these compounds with those of the corresponding *isobutyl* derivatives indicates that the loss of two hydrogen atoms accompany-

ing the conversion of $\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} > \text{C}$ into $\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} > \text{C}$ produces an increase of 21—27° in the boiling point.

J. J. S.

Carbamide as the Product of Oxidation of Nitrogenous Substances. By ADOLF JOLLES (*J. pr. Chem.*, 1901, [ii], 63, 516—522. Compare this vol., i, 30, 262).—The experiments on the oxidation of amides by means of permanganate (*loc. cit.*) are continued. Lactamide and succinamide, when oxidised, yield the whole of their nitrogen as carbamide. Although from aspartic acid (*loc. cit.*) and benzamide carbamide is not produced, yet the whole of the nitrogen of benzoylaspartic acid is quantitatively converted into carbamide in the oxidation.

In the experiments, the amide is oxidised by permanganate in the presence of very dilute sulphuric acid. The total nitrogen in the liquid is determined, and the carbamide precipitated as oxalate, and estimated.

K. J. P. O.

Condensation of Acetone and Carbamide. By ARTHUR WEINSCHENK (*Ber.*, 1901, 34, 2185—2187).—*Triacetonedicarbamide*, $\text{CMe}_2(\text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CMe}_2)_2$, obtained by passing hydrogen chloride into acetone in which carbamide is suspended and boiling for 7 hours, crystallises (with $3\text{H}_2\text{O}$) in leaflets, melts at 265—268°, and, when heated at 140—150° with water, is decomposed into ammonia, acetone, and carbon dioxide.

R. H. P.

The Thiocarbimide from the Seeds of Brassica Napus (Colza). By B. SJOLLEMA (*Rec. trav. Chim.*, 1901, 20, 237—242).—A crotonylthiocarbimide is obtained when colza seeds are freed from oil, treated with myrosin and water, and finally distilled in steam. It is an oil boiling at about 174° and having a sp. gr. 0.9933 at 11°/4°; it is optically inactive, and on treatment with alcohol and ammonia yields a crotonylthiocarbimide melting at 64°. This product does not appear to be identical with either of the compounds described by Hofmann (this Journ., 1874, 792) and Charon (*Abstr.*, 1899, i, 849).

J. J. S.

Existence of Derivatives of Quadrivalent Nitrogen. II. By OSCAR PILOTY and B. GRAF SCHWERIN (*Ber.*, 1901, 34, 2354—2367. Compare this vol., i, 517).—Both porphyrexin and porphyrexide are converted by the action of chlorine into a mono- and a di-chloroporphyraxide.

Chloroporphyraxide, $\text{C}_5\text{H}_8\text{ON}_4\text{Cl}$, prepared by the action of a concentrated solution of bleaching powder on an aqueous suspension of porphyrexide, crystallises in rhombic plates melting and decomposing at 152°, which are wine-red by transmitted light, and of a greenish-golden, metallic colour by reflected light. The mol. weight determined in acetic acid corresponded with the above formula. Concentrated nitric acid converts it into an ochre-yellow, crystalline mass, which is probably the nitrate; with water, the original chloroporphyraxide is immediately regenerated. It dissolves in sodium hydroxide and ammonia, forming a deep cherry-red solution. The *silver* salt, $\text{C}_5\text{H}_7\text{ON}_4\text{ClAg}$, prepared from the solution of the ammonium salt, forms a carmine-red, crystalline powder decomposing at 170°.

Dichloroporphyræxide, $C_5H_7ON_4Cl_2$, prepared by the action of chlorine on porphyræxide suspended in water, forms a red powder melting and decomposing at $117-118^\circ$, and readily soluble in ether or chloroform. The mol. weight, determined in benzene, corresponded with the above formula. In the moist state, it is rapidly converted into the monochloro-derivative, with evolution of chlorine. All the basic properties of porphyræxide have disappeared, and with concentrated nitric acid the nitrate (?) of monochloroporphyræxide is formed with evolution of chlorine. With concentrated ammonia, this compound explodes. Despite its instability, it dissolves in dilute ammonia or sodium hydroxide, forming salts. The *sodium* salt crystallises in deep violet-blue, rhombic plates melting and exploding at 145° ; with dilute sulphuric acid, dichloroporphyræxide is reformed. The *ammonium* salt forms sparingly soluble needles of deep violet colour, closely resembling murexide crystals, and decomposing violently at 96° . The *silver* salt forms a nearly black powder exploding at 150° , and is neither decomposed by light nor by long keeping.

The two chloroporphyræxides, as well as porphyræxide, react with hydrogen peroxide, evolving oxygen both in acid and alkaline solution; with hydrochloric acid, chlorine is evolved; with hydrogen sulphide, sulphur is set free; with hydriodic acid, iodine is liberated and porphyræxine formed. Quantitative experiments show that 1 mol. of porphyræxide liberates from hydriodic acid 1 atom of iodine; 1 mol. of chloroporphyræxide 3 atoms of iodine; and 1 mol. of dichloroporphyræxide 5 atoms of iodine. Each atom of chlorine sets free 2 atoms of iodine. This fact, with others, shows that the chlorine atoms have replaced hydrogen which was attached to nitrogen atoms.

The authors discuss the constitution of porphyræxide, and from the fact that it has a molecular weight, expressed by the formula $C_5H_7ON_4$, and from its relation to porphyræxine and to the two chloroporphyræxides, and finally from its behaviour towards reducing agents (hydriodic acid), conclude that it contains the group $(:N:O)$, in which nitrogen is quadrivalent. It may be represented by one of the formulæ $NH_2 \cdot C(CN) < \begin{smallmatrix} NH \\ CMe_2 \end{smallmatrix} > N:O$ or $\begin{smallmatrix} NH \cdot C(NH) \\ NH: C - CMe_2 \end{smallmatrix} > N:O$. Porphyræxide is consequently a derivative of nitrogen peroxide, and exhibits many properties resembling those of this substance. K. J. P. O.

Ammonia Nickel Cyanide. By A. BERNOULLI and E. GRETHNER (*Chem. Zeit.*, 1901, 25, 436-437).—A solution of nickel cyanide in concentrated ammonia, when kept, yields large, violet-blue, flat needles which quickly become transformed into paler and smaller needles having the composition $NiC_2N_2, 2NH_3, H_2O$. When heated at 250° , this is converted into nickel cyanide; it is only slowly decomposed by water or dilute acids, and is soluble in ammonium hydroxide, carbonate, sulphide, or oxalate, and also in potassium cyanide solution. J. J. S.

Influence of Light on the Decomposition of Aqueous Solutions of Potassium Ferricyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, 25, 522-523. Compare this vol., i, 455).—Solutions of

potassium ferrieyanide containing 5 grams or less of the salt in 100 grams of water follow the generalisation previously given.

The decomposition is complete in all cases, that is, all the iron may be precipitated as ferric hydroxide under the influence of sunlight. The rate of decomposition is greater the brighter the sunlight.

J. J. S.

Derivatives of *m*-Dibromodinitrobenzene. By C. LORING JACKSON and WALLACE P. COHOE (*Amer. Chem. J.*, 1901, 26, 1—9).—When bromine is added to bromoacetanilide suspended in water, *s*-tribromoaniline is produced, whilst by the action of bromine on the same substance suspended in glacial acetic acid or chloroform, a good yield of dibromoacetanilide is obtained. If dibromoaniline, prepared by the hydrolysis of dibromoacetanilide, is treated with nitrous acid, dibromobenzene is produced, which, on nitration, yields 1:3-dibromo-4:6-dinitrobenzene melting at 117°. By the action of aniline at 100° on dibromodinitrobenzene, 4:6-dinitro-1:3-dianilinobenzene is formed, identical with that obtained by Nietzki and Schedler (*Abstr.*, 1897, i, 464) from 1:3-dichloro-4:6-dinitrobenzene.

Bromodinitroanilinobenzene, $\text{NHPh}\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2$, obtained by the action of aniline on well-cooled dibromodinitrobenzene, is soluble in benzene, toluene, or chloroform, and occurs in two modifications; the yellow modification crystallises in short, thick, flat prisms or rhombic plates and melts at 157°, whilst the red modification forms square prisms, and, when heated to 135°, is completely converted into the yellow form. If a solution of the yellow form in benzene is allowed to evaporate, a red oil is deposited, which, on stirring, solidifies to crystals of the red modification.

When *m*-dibromodinitrobenzene is treated with sodium ethoxide, dinitroresorcinol diethyl ether is produced. *Dinitroresorcinol diphenyl ether*, $\text{C}_6\text{H}_2(\text{OPh})_2(\text{NO}_2)_2$, obtained by the action of sodium phenoxide on dibromodinitrobenzene, crystallises in slender, white prisms, melts at 129°, and is soluble in benzene, toluene, or chloroform; when this compound is dissolved in alcoholic ethyl sodiomalonate, phenol is eliminated, and *ethyl phenoxydinitrophenylmalonate*,

$\text{OPh}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$, is obtained as a pale yellow oil which yields a bright red *sodium* derivative.

When dibromodinitrobenzene is reduced with zinc dust and acetic acid, 1:3-dibromo-4:6-phenylenediamine is produced, identical with that obtained by Jackson and Calvert (*Abstr.*, 1896, i, 538) by the action of bromine on *m*-phenylenediacetamide. E. G.

Action of Sodium Sulphite on Tribromodinitrobenzene and Tribromotrinitrobenzene. By C. LORING JACKSON and RICHARD B. EARLE (*Amer. Chem. J.*, 1901, 26, 46—55).—When an alcoholic solution of 1:3:5-tribromo-2:4-dinitrobenzene is boiled for 5 hours with sodium sulphite, 1:3-dibromo-4:6-dinitrobenzene is produced. If 1:3:5-tribromo-2:4:6-trinitrobenzene is treated in a similar manner, 1:3-dibromo-2:4:6-trinitrobenzene is obtained, which crystallises from benzene in pale yellow prisms with a slight greenish tinge, melts at 135°, and is soluble in ether, chloroform, acetone, or alcohol.

When dibromodinitrobenzene is heated with a mixture of fuming nitric and strong sulphuric acids, tribromodinitrobenzene is produced, together with a small quantity of dibromotrinitrobenzene. 1:2:3-*Tri-bromo-4:6-dinitrobenzene* crystallises in yellowish-white, rectangular plates, melts at 150°, and is soluble in benzene, ether, chloroform, glacial acetic acid, acetone, or alcohol.

By the action of sodium ethoxide on dibromotrinitrobenzene, styphnic diethyl ether is produced. Sodium ethoxide reacts with tribromodinitrobenzene with formation of *bromodinitroresorcinol ethyl ether*, $\text{OH}\cdot\text{C}_6\text{HBr}(\text{NO}_2)_2\cdot\text{OEt}$, which crystallises from alcohol in white, feathery needles, and melts at 78°; its *barium* salt is described. The bromodinitroresorcinol ethyl ether is accompanied by a small quantity of another *substance*, which crystallises in long, white needles, melts at 58°, and is probably the corresponding diethyl ether. E. G.

Symmetrical Tri-iodobenzene. By C. LORING JACKSON and G. E. BEHR (*Amer. Chem. J.*, 1901, 23, 55—61).—1:3:5-Tri-iodobenzene, prepared from tri-iodoaniline by means of the diazo reaction, crystallises from alcohol in long, white prisms, melts at 181°, sublimes readily, and is soluble in benzene, carbon disulphide, chloroform, ether, glacial acetic acid, ethyl acetate, alcohol, or acetone; it is identical with the compound obtained by Istrati and Georgescu (*Abstr.*, 1892, 1310) by heating together benzene, iodine, and concentrated sulphuric acid, and regarded by them as 1:2:3-tri-iodobenzene. When tri-iodobenzene is treated with fuming nitric acid, it yields tri-iododinitrobenzene, which melts at 210°, and is converted by aniline into trianilinodinitrobenzene, identical with that obtained by Palmer and Jackson (*Abstr.*, 1890, 248) from 1:3:5-tribromo-2:4-dinitrobenzene. E. G.

Syntheses in the Diphenyl Series. By FRITZ ULLMANN and JEAN BIELECKI (*Ber.*, 1901, 34, 2174—2185).—Very good yields of symmetrically substituted diphenyl compounds can be obtained by heating haloid derivatives of the benzene hydrocarbons, either alone or dissolved in nitrobenzene, with copper powder; for example, *o*-bromonitrobenzene, when heated with copper powder, yields 2:2'-dinitrodiphenyl. The following new compounds are described: 3:3':4:4'-*tetranitrodiphenyl* (prepared from 4-iodo-1:2-dinitrobenzene, obtained by the nitration of *m*-iodonitrobenzene, and forming yellow crystals melting at 74.5°), which crystallises in yellow prisms and melts at 186°; 2:2':4:4':6:6'-*hexanitrodiphenyl* (from picryl chloride), which forms large, brownish crystals (with $\frac{1}{2}\text{C}_6\text{H}_5\text{Me}$) melting at 238°; 4:4'-*dichloro-2:2'-dinitrodiphenyl* (from 1:4-dichloro-2-nitrobenzene), which forms yellow crystals melting at 136°, and the analogous *bromo*-derivative, which crystallises in yellow needles melting at 138°; *methyl 2:2'-dinitrodiphenyl-4:4'-dicarboxylate* (from *methyl 4-bromo-3-nitrobenzoate*, crystallising in large, lustrous needles and melting at 104°), which crystallises in large prisms and melts at 159—160°; *methyl 2:2':6:6'-tetranitrodiphenyl-4:4'-dicarboxylate* (from *methyl 4-chloro-3:5-dinitrobenzoate*, melting at 175°), which crystallises in colourless needles and melts at 173°. A 74 per cent. yield of 1:1'-dinaphthyl is obtained by heating α -iodonaphthalene with copper powder. R. H. P.

Electrolytic Reduction of Aromatic Nitro compounds to Amines. By A. CHILESOTTI (*Zeit. Elektrochem.*, 1901, 7, 768—773).—The nitro-compound is made into an emulsion with hydrochloric or sulphuric acid of sufficient strength to leave the solution 0·7 to 0·8*N* after reduction is complete. This emulsion is placed in a jar with a cathode of nickel gauze. A porous pot contains the lead anode immersed in 9 per cent. sulphuric acid. A current density of about 0·12 ampere per sq. cm. is employed. The temperature rises to 40—50°. To the cathode solution, a little tin, copper, or iron salt is added. The tin salts give the best results. The yields, as regards both current and material, are almost quantitative. The spongy metal which is deposited on the cathode during the reduction is the active agent. A cathode of copper gauze without added salt gives a very incomplete reduction. The fact that copper gives almost as good results as tin shows that the metals do not act primarily on the nitro-compounds, which are hardly reduced by copper. It is also improbable that the nitroso-compound which is the first reduction product is acted on, because it is found that by the action of finely divided copper, nitrosobenzene yields large quantities of azoxy- and azo-benzene in addition to aniline. Phenylhydroxylamine is, however, very rapidly reduced to aniline by finely divided copper. The author therefore supposes that the nitro-compounds are first reduced to the corresponding hydroxylamine derivatives, as is always the case, and that these are then very rapidly reduced to amines by the spongy metals. The metals of course go into solution, but are immediately reprecipitated by the current. T. E.

Oxidation of Benzylamine. By EUGEN BAMBERGER and THOR SCHEUTZ (*Ber.*, 1901, 34, 2262—2272. Compare Abstr., 1899, i, 347, 682; this vol., i, 200).—The oxidation of fatty bases, such as benzylamine, ethylamine, &c., by Caro's reagent, proceeds much more slowly than that of aromatic bases, and is also much slower than that of the first products of the oxidation, so that it is difficult to obtain the latter in any quantity. In the case of benzylamine, the chief product is benzoic acid, in addition to which the following have been isolated: benzaldoxime, benzonitrile, benzhydroxamic acid, phenylnitroethane, and benzaldehyde. Indications of the presence of benzamide and phenylnitrolic acid were also obtained, and three neutral substances melting at 205°, 100—103°, and about 100°, and a colourless base, which forms yellow solutions in acids, were isolated.

It appears probable that the first stage of the oxidation consists in the formation of benzyhydroxylamine, which, however, at once passes by oxidation into benzaldoxime. This seems to constitute the typical distinction between the behaviour of aromatic and fatty bases towards Caro's reagent. The aromatic bases yield the corresponding hydroxylamine, which is then further oxidised to a nitroso-compound and finally to a nitro-compound.

The benzaldoxime is then partly converted into benzonitrile, partly into benzohydroxamic acid, and partly into isophenylnitromethane, $\text{CHPh}\cdot\text{NO}_2\text{H}$, which at once passes into phenylnitromethane, $\text{CH}_2\text{Ph}\cdot\text{NO}_2$.

The production of benzonitrile in this reaction supplies the converse of Mendius' well known reduction of the nitriles to amines. A. H.

Nitro- and Bromo-derivatives of the Xylidines. By EMILIO NOELTING, A. BRAUN, and G. THESMAR (*Ber.*, 1901, 34, 2242—2262).—Both *o*-3- and *o*-4-xylidine yield, on nitration, all three possible mononitro-derivatives, whilst Noelting and Stoecklin (*Abstr.*, 1891, 692) previously only obtained two of these from each base. The statements previously made are therefore to be replaced by those now published. The nitro-derivatives of *o*-3-xylidine may be obtained either by nitrating the corresponding acetylxylylidide or by the direct nitration of the base at a low temperature in presence of sulphuric acid. In the former case, the separation of the three products may be carried out by distillation with steam and is very tedious, the relative proportions formed being 30 per cent. of 4-, 13 per cent. of 5-, and 55 per cent. of 6-nitro-*o*-3-xylidine. The yield obtained by direct nitration varies, the amount of 5-nitro-compound increasing with the amount of sulphuric acid employed. Using 20 parts of sulphuric acid, there was formed 25 per cent. of 3-, 45 per cent. of 5-, and 30 per cent. of 6-nitro-compound. 4-Nitro-*o*-3-xylidine crystallises in brick-red, lozenge-shaped tablets melting at 118—119°, and only dissolves in concentrated hydrochloric acid. The *acetyl* derivative crystallises in colourless needles melting at 160°, and the *benzoyl* derivative melts at 177—178°. 5-Nitro-*o*-3-xylidine crystallises in light yellow needles melting at 111—112°, and has more strongly basic properties than the foregoing compound. The *acetyl* derivative crystallises in needles melting at 230—231°, whilst the *benzoyl* derivative melts at 227—228°. 6-Nitro-*o*-3-xylidine forms brownish-yellow prisms melting at 114°. The *acetyl* derivative crystallises in faintly yellow needles melting at 149—150°, and the *benzoyl* derivative melts at 208—209°.

o-4-Xylidine also yields three mononitro-derivatives, the relative proportions, when the nitration is carried out in presence of sulphuric acid, being 47 per cent. of 5-, 31 per cent. of 3-, and 13 per cent. of 6-nitro-*o*-4-xylidine. 5-Nitro-*o*-4-xylidine crystallises in brownish-red prisms melting at 139—140°, and forms salts which are decomposed by water. The *acetyl* derivative crystallises in small, light yellow needles melting at 107°, and the *benzoyl* derivative in light yellow, silky needles melting at 149—150°. 3-Nitro-*o*-4-xylidine crystallises in scarlet-red prisms melting at 65—66°, and is readily volatile with steam. The *acetyl* derivative forms small needles melting at 115—116°, and the *benzoyl* compound sparingly soluble needles melting at 199—200°. 6-Nitro-*o*-4-xylidine crystallises in long, lustrous, orange-coloured plates melting at 74—75°. The *acetyl* derivative crystallises in small needles melting at 209—210°, whilst the *benzoyl* derivative melts at 223—224°.

The four isomeric xylylenediamines can all be prepared by the reduction of the mononitro-*o*-xylidines. *o*-3:4-Xylylenediamine crystallises in colourless plates melting at 89°, and, like the other isomerides, is quite stable in the air when dry. *o*-4:5-Xylylenediamine also forms plates, and melts at 125—126°, whilst *o*-3:5-xylylenediamine crystallises in small needles melting at 66—67°, and *o*-3:6-xylylenediamine

separates in faint brown-coloured prisms melting at 116° , and can also be prepared by treating *o*-3-xylidine with diazobenzene-*m*-sulphonic acid and decomposing the azo-compound produced with tin and hydrochloric acid.

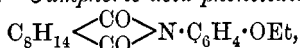
Monobromo-derivatives of m-4-xylidine.—6-Bromo-*m*-4-xylidine has previously been prepared by Genz (*Ber.*, 1870, 3, 225), and can also be obtained from 4-nitro-*m*-6-xylidine by replacing the amino-group by bromine and then reducing. It melts at 99 – 100° , whilst the *acetyl* derivative melts at 168 – 179° . The *p*-nitrobenzylidene derivative, $C_6H_2BzMe_2 \cdot N : CH \cdot C_6H_4 \cdot NO_2$, forms yellow needles melting at 139° . The corresponding 6-bromo-*m*-4-xylidene crystallises in colourless needles melting at 72° . 2-Bromo-*m*-4-xylidine is prepared from 4-nitro-*m*-2-xylidine in a similar manner to the foregoing compound. 2-Bromo-4-nitro-*m*-xylene crystallises in soft, light yellow needles which melt at 57 – 58° . 2-Bromo-*m*-4-xylidine crystallises in long, colourless, silky needles melting at 47 – 48° . The *acetyl* derivative melts at 151 – 152° , and the *p*-nitrobenzylidene derivative at 182 – 183° . The corresponding 2-bromo-*m*-4-xylidene crystallises in light yellow needles melting at 68° . 5-Bromo-*m*-4-xylidine, also melting at 47 – 48° , is formed by the direct bromination of *m*-4-xylidine, and has previously been described by Fischer and Windaus (*Abstr.*, 1900, i, 484), who proved its constitution by converting it into mesitylenic acid. The *acetyl* derivative melts at 196 – 197° , the *p*-nitrobenzylidene derivative at 130° , and the corresponding 5-bromo-*m*-4-xylidene at 72° . 5-Bromo-*m*-4-xylidine can be prepared indirectly by two methods, each of which shows its constitution. 4-Nitro-*m*-6-xylidine yields, on bromination, 5-bromo-4-nitro-*m*-6-xylidine, which crystallises in large prisms melting at 66 – 67° . 5-Bromo-4-nitro-*m*-xylene, prepared from the foregoing by elimination of the amino-group, crystallises in flat, faintly yellow needles melting at 39 – 40° , and is converted by reduction into the desired 5-bromo-*m*-4-xylidine. According to the second method, 4-nitro-*m*-5-xylidine is converted by the diazo-reaction into the corresponding 5-bromo-derivative, and this, on reduction, yields the 5-bromo-*m*-4-xylidine.

Bromo-derivatives of m-2-xylidine.—4-Bromo-*m*-2-xylidine is best prepared synthetically from 2-nitro-*m*-xylene, which is converted by nitration into 2:4-dinitro-*m*-xylene, and on reduction with alcoholic ammonium sulphide, this compound yields 2-nitro-4-amino-*m*-xylene, which crystallises in long, golden, lustrous needles melting at 81 – 82° , and is readily converted by the diazo-reaction into 4-bromo-2-nitro-*m*-xylene, crystallising in yellowish prisms melting at 70 – 71° . Finally, this compound yields on reduction 4-bromo-*m*-2-xylidine, which forms lustrous, colourless needles melting at 21.5° to a colourless oil which boils at 146 – 147° under 15 mm. pressure. The *acetyl* derivative, crystallising in small needles melting at 136° , is best prepared indirectly from 4-nitro-*m*-2-acetylxylylidene, which is converted by reduction and replacement of the resulting amino-group by bromine into this compound; it was, however, found impossible to prepare the free base from it by hydrolysis.

5-Bromo-*m*-2-xylidine, which is the only remaining isomeride, has been previously prepared by Fischer and Windaus (*loc. cit.*), who, however, did not ascertain its constitution. The bromination of *m*-2-acetyl-

xylylide leads to the formation of a mixture of 4- and 5-bromo-derivatives. A. H.

Camphoric Acid Phenetide. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1901, 25, 445).—*Camphoric acid phenetide*,



is obtained when the product formed by the action of camphoric acid on *p*-phenetidine is crystallised several times from water and alcohol. It crystallises in plates, melts at 112°, and may probably be of use in cases of tuberculosis. J. J. S.

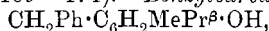
Orientating influence of the Methoxy-group on the Nitro-group. By FELIX KAUFER and FRANZ WENZEL (*Ber.*, 1901, 34, 2238—2242).—Whilst the presence of a nitro-group in the benzene nucleus favours the entrance of a second nitro-group in the meta-position, that of a hydroxyl group favours the production of ortho- and para-compounds. When both groups are present simultaneously, the influence of the hydroxyl group preponderates, and ortho- and para-dinitro-compounds are obtained by nitration. The following experiments prove that the methoxy-group has the same directing influence as the hydroxyl group. *o*-Nitro-*p*-cresol methyl ether is readily converted by nitration in acetic acid solution into *dinitro-p-cresol methyl ether*, $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2 \cdot \text{OMe}$, which crystallises in colourless needles melting at 126—128°. On reduction, it yields *diamino-p-cresol methyl ether*, which crystallises in long, lustrous prisms melting at 72—73°.

13-Methoxy 10-methylphenanthrazine, $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}_{14}\text{H}_8$, is obtained when the base is treated with phenanthraquinone, and crystallises in light yellow, lustrous needles melting at 265—268°.

8-Methoxy-2:3:5-trimethylquinoxaline, $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me} \begin{array}{c} \text{N}:\text{CMe} \\ \diagup \quad \diagdown \\ \text{N}:\text{CMe} \end{array}$, is obtained by the action of diacetyl on the base, and crystallises in thin, colourless needles melting at 125°. The constitution of the dinitro-compound must therefore be

$\text{C}_6\text{H}_2\text{Me}(\text{OMe})(\text{NO}_2)_2$ [$\text{Me}:\text{NO}_2 \cdot \text{NO}_2 \cdot \text{OMe} = 1:2:3:4$], so that the second nitro-group has entered in the ortho-position to the one already present. *p*-Nitro-*o*-cresol methyl ether is not acted on by concentrated nitric acid alone, but in the presence of sulphuric acid yields *trinitro-o-cresol methyl ether*, which crystallises in long, colourless needles melting at 111—112°. This compound is the methyl ether of Noelting's trinitro-*o*-cresol (*Abstr.*, 1884, 1007), and must contain at least two nitro-groups in the ortho-position to one another. A. H.

Benzylcarvacrol and Benzyl-*m*-cresol. By G. ANTONIO VENTURI (*Gazzetta*, 1901, 31, i, 469—474).—*Benzylcarvacrol*,



obtained by the action of benzyl alcohol on carvacrol in presence of zinc chloride, boils at 235—240° under 50 mm. pressure. Its *acetyl* derivative, $\text{C}_{19}\text{H}_{22}\text{O}_2$, is a dense, oily, pale yellow liquid boiling at 230° under 30 mm. pressure.

Benzyl-m-cresol, $\text{CH}_2\text{Ph} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}$, separates from benzene in

acicular crystals melting at 93—93.5°. Its *acetyl* derivative, $C_{16}H_{16}O_2$, is deposited from light petroleum in tabular crystals melting at 46.5°.

T. H. P.

Nitration of Ortho- and Meta-chloro- and -bromo-benzoic Acids. By ARNOLD F. HOLLEMAN and B. R. DE BRUYN (*Rec. trav. Chim.*, 1901, 20, 206—234. Compare Rhalis, *Annalen*, 1879, 198, 109).—*o*-Chlorobenzoic acid, when added to nitric acid of sp. gr. 1.52 at the ordinary temperature, yields a mixture of 2-chloro-5-nitro- with a little 2-chloro-3-nitro-benzoic acid. The two acids are best separated by fractional crystallisation of their potassium salts from concentrated aqueous solutions. 2-Chloro-3-nitrobenzoic acid melts at 185°, is only sparingly soluble in water, and when heated with alcoholic ammonia in sealed tubes, yields Hübner's 3-nitro-2-aminobenzoic acid (*Annalen*, 1879, 195, 37).

o-Bromobenzoic acid, when treated in the same manner, yields 2-bromo-5-nitrobenzoic acid melting at 180° (compare Rhalis, *loc. cit.*), and 2-bromo-3-nitrobenzoic acid melting at 191°.

m-Chlorobenzoic acid yields a mixture of 3-chloro-6-nitrobenzoic acid melting at 139° and 3-chloro-2-nitrobenzoic acid melting at 235°; the two acids are best separated by fractional crystallisation from ether, when crystals of the chief product, the 3:6-acid, are obtained, the ethereal mother liquor is evaporated, and the dry residue extracted several times with small amounts of warm benzene and finally crystallised from alcohol.

When dilute hydrochloric acid is added to a cold solution of potassium 3-chloro-6-nitrobenzoate, an *acid potassium* salt, $C_{14}H_7O_8N_2Cl_2K$, separates.

m-Bromobenzoic acid yields as its chief product of nitration 3-bromo-6-nitrobenzoic acid melting at 140°, together with 3-bromo-2-nitrobenzoic acid melting at 250°. The two acids are separated by fractional crystallisation from cold dilute alcohol (65 per cent. by vol.) and subsequent crystallisation of the sodium salts from water. The 3-bromo-6-nitro-acid forms definite compounds with benzene and its homologues.

The determinations of the amount of each isomeride formed in the different cases has been made by taking the solidifying point, and comparing it with the solidifying point of mixtures of known composition. The paper concludes with a criticism on the rules for substitution in the benzene nucleus.

J. J. S.

Structure of Kalle and Co.'s *o*-Chlorodinitrobenzoic Acid. By ARNOLD F. HOLLEMAN (*Rec. trav. Chim.*, 1901, 20, 235—236).—Kalle and Co.'s *o*-chlorodinitrobenzoic acid (*Chem. Centr.*, 1900, i, 742) may be obtained by the nitration of 2-chloro-3-nitrobenzoic acid and also of the 2-chloro-5-nitro-acid, and must hence be 2-chloro-3:5-dinitrobenzoic acid.

J. J. S.

Action of Formaldehyde on Methyl *o*-Aminobenzoate. By HUGO ERDMANN (*J. pr. Chem.*, 1901, [ii], 63, 569—572. Compare this vol., i, 536).—Mehner (this vol., i, 470) obtained from methyl *o*-aminobenzoate and formaldehyde methyl methylenedi-*o*-aminodibenzoate, whilst the author (*loc. cit.*) observed the formation of methyl methylene-*o*-aminobenzoate. The author finds that the reaction takes place in three stages; first, methyl

methylene-*o*-aminobenzoate is formed; 2 mols. of this substance then interact with elimination of formaldehyde, and the formation of a compound, $C_{17}H_{18}O_4N_2 \cdot H_2O$, which is obtained by crystallising from dilute alcohol, the crude product of the action of formaldehyde on methyl *o*-aminobenzoate, and separates in needles melting at 117° . This compound is then transformed into the methylenediamino-compound described by Mehner. The conditions by which this transformation is effected could not be exactly determined. K. J. P. O.

Action of Pure Nitric Acid on the three Toluic Acids and on their Derivatives. By L. VAN SCHERPENZEEL (*Rec. trav. Chim.*, 1901, 20, 149—182).—When *p*-toluic acid is nitrated at 0° , it yields 2-nitro-*p*-toluic acid, $[Me:NO_2:CO_2H = 1:2:4]$, and at the ordinary temperature, 2:6-dinitro-*p*-toluic acid. The methyl ester, amide, and methylamide, when nitrated at 0° , yield derivatives of the 2-nitro-acid. The methylamide of *p*-toluic acid melts at $145\text{--}145.5^\circ$ (compare Gattermann and Schmidt, *Abstr.*, 1887, 358). The dimethylamide forms large, transparent crystals melting at 41° and distilling at 156° under 10 mm. pressure, and is readily soluble in most organic solvents. The methylamide of 2-nitro-*p*-toluic acid melts at 149° , and is readily soluble in hot water. When methyl *p*-toluate is nitrated at 20° , the product is methyl 2-nitro-*p*-toluate; *p*-toluamide at 20° yields the mononitro-acid, but the methylamide yields the 2:6-dinitro-acid, and the dimethylamide yields the dimethylamide of the dinitro-acid.

m-Toluic acid was prepared and purified by Ador and Rilliet's method (*Ber.*, 1879, 12, 2300), a bye-product in the preparation of the acid is 6-nitro-*m*-toluic acid. *m*-Toluyyl chloride melts at -23° , the methyl ester boils at $220.5\text{--}221^\circ$, Klages gives $214\text{--}215^\circ$ (*Abstr.*, 1899, i, 599), the amide forms scintillating crystals melting at $93\text{--}94^\circ$, the methylamide melts at $44.5\text{--}45^\circ$, and the dimethylamide is an oil distilling at 148° and having sp. gr. 1.043 at 15° . When nitrated at 0° , *m*-toluic acid yields a mixture of 4-nitro-*m*-toluic acid melting at 223° and 2-nitro-*m*-toluic acid melting at $184\text{--}185^\circ$ (Jacobsen, *Abstr.*, 1882, 185); the methyl ester, amide, and methylamide yield the derivatives of the two mono-nitro-acids, but the dimethylamide yields the dimethylamide of the 4-nitro-acid only. When nitrated at the ordinary temperature, the meta-acid yields 2:4-dinitro-*m*-toluic acid melting at 173° ; this acid is also formed when the amide and methylamide of *m*-toluic acid or of 4-nitro-*m*-toluic acid are nitrated at the ordinary temperature. Methyl *m*-toluate, on nitration at the ordinary temperature, yields methyl 2:4-dinitro-*m*-toluate melting at $104\text{--}105^\circ$, but the dimethylamide of *m*-toluic acid yields the dimethylamide of 4-nitro-*m*-toluic acid.

Methyl 4-nitro-*m*-toluate melts at 71.5° , the amide crystallises in glistening needles melting at 191° , the methylamide in colourless plates melting at $135\text{--}136^\circ$ and only sparingly soluble in ether, and the dimethylamide in colourless crystals melting at 88.5° and readily turning red on exposure to sunlight. The amide of 2-nitro-*m*-toluic acid melts at $135\text{--}136^\circ$.

Methyl *o*-toluate distils at 213° [Kellas (*Abstr.*, 1898, i, 86) gives $207\text{--}208^\circ$] and has the sp. gr. 1.073 at 15° . The methylamide crys-

tallises in colourless needles melting at 75° , the *dimethylamide* is a colourless liquid distilling at 147° and having the sp. gr. 1.033 at 25° . When nitrated at 0° , *o*-toluic acid yields a mixture of 4-nitro-*o*-toluic acid melting at $178-178.5^{\circ}$ (compare Jacobsen and Wierss, Abstr., 1883, 1121) and 6-nitro-*o*-toluic acid melting at $184-184.5^{\circ}$; the latter is probably identical with Jacobsen and Wierss' β -nitro-acid melting at 145° . The two acids are best separated by fractional crystallisation of their methyl esters from methyl alcohol. The methyl ester, amide, methylamide, and dimethylamide of *o*-toluic-acid also yield the corresponding derivatives of the 4- and 6-nitro-acids when nitrated at 0° . When nitrated at the ordinary temperature, *o*-toluic-acid, as well as its two mononitro-derivatives, yields 4:6-dinitro-*o*-toluic acid (compare Jacobsen and Wierss, *loc. cit.*). The methyl ester under similar conditions yields methyl 4:6-dinitro-*o*-toluate melting at $73-73.5^{\circ}$. The amide and methylamide yield the 4:6-dinitro-acid, but the dimethylamide gives the 4-nitro-acid.

4-Nitro-*o*-toluoyl chloride crystallises in colourless needles melting at $59-60^{\circ}$ and not readily decomposed by water, the *methyl ester* crystallises in oblong prisms and melts at 69° , the *methylamide* forms slender needles melting at 160° , and the *dimethylamide* melts at $105-106^{\circ}$. 6-Nitro-*o*-toluoyl chloride melts at $68-68.5^{\circ}$; the *methyl ester* forms pale yellowish needles melting at 66° , the *amide* colourless needles melting at 163° , the *methylamide* melts at $131-132^{\circ}$, and the *dimethylamide* at $69.5-70^{\circ}$.

J. J. S.

New Bismuth Salicylate. By PAUL THIBAUT (*J. Pharm.*, 1901, [vi], 14, 22-25).—Bismuthic oxide, when treated on the water-bath with a strong solution of salicylic acid, yields *bismuth salicylate*, $\text{Bi}_2\text{O}_3(\text{C}_7\text{H}_5\text{O}_3)_3$, which crystallises in small, transparent prisms; when treated with warm water, boiling alcohol or ether, it yields salicylic acid, and, when fused, phenol.

R. H. P.

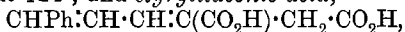
Reduction of Indigotin in an Anhydrous Medium. By ARTHUR BINZ (*J. pr. Chem.*, 1901, [ii], 68, 497-516).—On heating indigotin in boiling naphthalene with zinc dust in the absence of oxygen, the blue solution rapidly becomes emerald-green. With completely anhydrous zinc dust or zinc amalgam, the same change occurs. On extracting the product in a specially adapted Soxhlet apparatus with boiling naphthalene in the absence of oxygen, the extract is at first green and later colourless. The latter extract becomes deep blue when air is admitted, and contains a substance yielding indigotin and zinc oxide. In order to determine the nature of this colourless substance, the action of boiling naphthalene on indigo-white or zinc indigo-white has been studied. Indigo-white dissolves in molten naphthalene with a red colour, and is converted into a substance which cannot again be oxidised to indigotin. *Zinc indigo-white*, $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2\text{Zn}(\text{?})$, prepared from calcium indigo-white and zinc chloride, and crystallising in lustrous leaflets, was extracted with boiling naphthalene; after the indigotin accompanying the zinc indigo-white had been removed, phenomena were observed identical with those previously described in the extraction of the product of the action of zinc dust on indigotin in boiling naphthalene. Zinc indigo-white is produced when indigo-white and zinc

oxide are heated in boiling naphthalene; the solution thus obtained is emerald-green. The author concludes that zinc indigo-white is the chief product of the action of zinc dust on indigotin in boiling naphthalene. K. J. P. O.

Dibenzylidinitrile [4:4'-Dicyano-*s* diphenylethane]. By P. KATTWINKEL and RICHARD WOLFFENSTEIN (*Ber.*, 1901, 34, 2423—2425).—When *p*-toluonitrile is heated with aqueous potassium persulphate for 5—6 hours at 100°, 40 per cent. of it remains unchanged, and *p*-cyanobenzoic acid (7 per cent.) and 4:4'-dicyano-*s*-diphenylethane, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ (6 per cent.), are formed; the latter melts at 198°, and on hydrolysis with concentrated sulphuric acid yields the corresponding *s*-diphenylethane-4:4'-dicarboxylic acid, which does not melt at 320°.

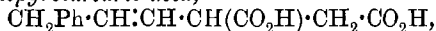
p-Cyanobenzoic acid, which Sandmeyer has described (*Abstr.*, 1885, 981) as melting at 214°, really melts at 219°; it can be crystallised from boiling water, and is not converted by this treatment into terephthalamic acid as stated by him. Sandmeyer's "terephthalamic acid" was only impure *p*-cyanobenzoic acid. W. A. D.

Attempted Synthesis of a $\gamma\delta$ -Unsaturated Acid. By FRITZ FICHTER and SYLVAIN HIRSCH (*Ber.*, 1901, 34, 2188—2191).—An attempt to obtain a γ -unsaturated acid by the partial reduction of an acid containing two double linkings in the β - and δ -positions. Cinnamaldehyde condenses with ethyl succinate in the presence of sodium ethoxide to form the hydrocarbon $\alpha\beta$ -diphenyl- $\alpha\gamma\eta$ -octatetrene, $\text{CHPh}\cdot\text{CH}\cdot[\text{CH}\cdot\text{CH}]_2\cdot\text{CH}\cdot\text{CHPh}$, which crystallises in transparent tablets melting at 124°, and styrylitaconic acid,

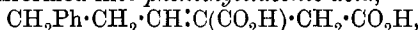


which crystallises in lustrous, felted needles, melts and decomposes at 215—218°, and forms a microcrystalline calcium salt.

Phenethylidenepyrotartaric acid,



obtained by reducing styrylitaconic acid in the cold with sodium amalgam, crystallises in tablets or needles, melts at 112°, forms crystalline calcium and barium salts, and when neutralised and boiled for 30 hours is transformed into phenethylitaconic acid,



which crystallises in clusters of lustrous needles melting at 153° and forms an amorphous calcium salt. The latter acid, when reduced in warm acid solution with sodium amalgam, yields phenethylpyrotartaric acid, $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises in clusters of needles and melts at 83°. R. H. P.

Action of Sulphuryl Chloride on Ethyl Gallate. By GIROLAMO MAZZARA and P. GUARNIERI (*Gazzetta*, 1901, 31, i, 464—468).—Ethyl dichlorogallate, $\text{C}_6\text{Cl}_2(\text{OH})_3\cdot\text{CO}_2\text{Et}$, prepared by the action of sulphuryl chloride (2 mols.) on ethyl gallate (1 mol.), separates from water, with $1\frac{1}{2}\text{H}_2\text{O}$, in faintly nacreous, colourless laminae, melting at 121—128°, and showing a red tint when viewed in mass. After the removal of the water, the compound melts at 133—134°, at which temperature the long prismatic needles separating from benzene also melt. It dissolves slightly in chloroform, and is soluble also in dilute alkali carbonate

solutions, giving a yellowish liquid which assumes successively a violet and a dark red coloration. In aqueous solutions, it gives a turquoise coloration with ferric chloride. Attempts to obtain dichlorogallie acid from the ethyl ester gave negative results.

T. H. P.

Dihydroxyfluorescein. By CARL LIEBERMANN (*Ber.*, 1901, 34, 2299—2303).—Hydroxyquinol condenses with phthalic anhydride to form a *dihydroxyfluorescein*, $C_{20}H_{12}O_7$, which crystallises in lustrous, greenish-golden, microscopic leaflets and forms a crystalline *tetracetate* melting at 264° ; it dyes unmordanted wool and silk orange and gives good colours with mordanted cotton.

R. H. P.

Lichens and their Characteristic Constituents. VI. By OSWALD HESSE (*J. pr. Chem.*, 1901, [ii], 63, 522—553. Compare *Abstr.*, 1898, i, 531, 679; 1899, i, 381; this vol., i, 85, 149, 546).—*Usnea longissima* contains only *d*-usnic acid ($[\alpha]_D + 490.3^\circ$ at 15° in chloroform solution), and not *l*-usnic acid as found by Salkowski (this vol., i, 152). This acid is a phenolcarboxylic acid, which yields normal salts, $C_{18}H_{15}O_7M'$, and basic salts. The *barium* salt, $(C_{18}H_{15}O_7)_2Ba \cdot 4H_2O$, prepared from very dilute solutions of usnic acid and barium hydroxide, forms yellowish-white crystals, the basic *strontium* salt, $C_{18}H_{14}O_7Sr \cdot 2H_2O$, yellow prisms.

Usnidic acid, $C_{18}H_{15}O_8 \cdot 2H_2O$, prepared by fusing *d*-usnic acid for a very short time with potash, crystallises in white needles, which melt and decompose at 195° , and is a monobasic acid, giving in alcoholic solution a bluish-green coloration with ferric chloride, and readily oxidising in alkaline solution.

Alectoria jubata = *Bryopogon jubatum* var. *implexum* = *Alectoria implexa* = *Alectoria jubata* var. *cana* (gathered in the Tyrol), contains in the outermost cell-layers bryopogonic acid and in the inner alectoric acid; the mixture of these is Zopf's salazinic acid (*Abstr.*, 1898, i, 90). These two acids can be separated by acetic acid, in which alectoric acid is insoluble.

Bryopogonic acid, $C_{28}H_{22}O_{14}$, crystallises in small, colourless needles, decomposing at 260° , and in alcoholic solution gives a brownish-red coloration with ferric chloride. It is readily soluble in alkalis and alkali carbonates, the solutions quickly becoming dark red. *isoBryopogonic acid*, $C_{28}H_{22}O_{14}$, is formed when a solution of bryopogonic acid in potassium hydroxide is left to stand; hydrochloric acid precipitates the acid as a red, amorphous powder, which can be crystallised from acetic acid. It melts at a very high temperature and gives a dark brown coloration with ferric chloride in alcoholic solution.

Evernia furfuracea was found to contain no erythric or olivetoric acid (compare Zopf, this vol., i, 87), but together with atranorin a new monobasic acid, *evernuric acid*, $C_{22}H_{24}O_8$, crystallising in small, colourless needles melting at 191 — 192° ; its alcoholic solution gives a violet coloration with ferric chloride and a yellow with bleaching powder; when boiled with barium hydroxide, carbon dioxide is eliminated; and its ammoniacal solution gives a precipitate with barium chloride.

Parmelia acetabulum contains salazinic acid. On keeping a solution in potassium hydroxide, the *potassium* salt, $C_{28}H_{20}O_{12}K_4$, of rubidic acid is obtained as scarlet, prismatic crystals; *rubidic acid*, $C_{28}H_{24}O_{12}$, forms a brick-red powder which decomposes at a high temperature. A solution of the potassium salt oxidises in the air, yielding an acid, $C_{28}H_{20}O_{11}$, which forms hard, black lumps.

Parmelia glabra, from the Black Forest, contains lecanoric acid, (m. p. 166°).

Pannaria lanuginosa yields two acids, *hydroxyrocceic acid*, $C_{17}H_{32}O_5$, which crystallises in colourless, flattened needles melting at 128°, and is precipitated by barium hydroxide; and *pannaric acid*, $C_9H_8O_4 \cdot \frac{1}{2}$ or $2H_2O$, a monobasic acid, which crystallises in small, six-sided prisms melting at 224°, and is not precipitated by barium hydroxide; in alcoholic solution, it gives a blue coloration with ferric chloride, and with concentrated sulphuric acid yields a quinhydrone (?) as steel-blue needles.

Gyrophora polyphylla contains two acids, gyrophoric acid, which, with acetic acid yields orsellic acid, and, with alcohol, orcinol and ethyl orsellate; and umbilicaric acid, $C_{24}H_{16}O_6 \cdot OMe$, which crystallises in colourless leaflets melting at 185–186°, and with hydriodic acid yields methyl iodide and orcinol; the *potassium* salt, $C_{25}H_{20}O_{10}K_2 \cdot 5H_2O$, forms a colourless, crystalline powder. Boiling barium hydroxide converts it into orcinolcarboxylic and *umbilicarinic acid*, $C_{16}H_{12}O_6 \cdot OMe$, which crystallises in colourless needles melting and decomposing at 180°, and with ferric chloride gives a violet coloration.

Blastenia arenaria contains blastenin and phytosterol. *B. percrocata* contains blastenin, but no chrysophanic acid.

Urceolaria scruposa yields lecanoric and traces of a second acid.

Pertusaria corallina = *Pertusaria ocellata* β *corallina* = *Isidium corallinum* contains *ocellatic acid*, $C_{20}H_{15}O_{11} \cdot OMe$, which forms microscopic, crystalline aggregates melting and decomposing at 208°, and with ferric chloride gives a purple-violet coloration; the *potassium* salt forms colourless needles.

Pertusaria communis β *variolosa* contains *orbiculatic acid*, $C_{22}H_{36}O_7$, crystallising in colourless leaflets melting at 82°; it is monobasic, and does not give a coloration with ferric chloride. K. J. P. O.

Action of Bromoacetophenone on Sodioacetylacetone. By FR. MARCH (*Compt. rend.*, 1901, 133, 45–47).—A triketone *benzoyldiacetylthane*, $CH(OMe)_2 \cdot CH_2 \cdot CPh$, is obtained by the action of bromoacetophenone on sodioacetylacetone in presence of alcohol, and is separated by means of a compound, $C_{26}H_{26}O_6Cu$, which it forms with cupric acetate, and which can be crystallised from chloroform, although it is not very soluble in other organic solvents. This compound melts and decomposes at 219–220°, and is decomposed by sulphuric acid with liberation of the triketone. The triketone forms colourless crystals which melt at 57–58°, and dissolve in most ordinary organic solvents except light petroleum. When treated with alcoholic potash, the triketone yields acetic acid and the acetophenoneacetone described by Paal; with semicarbazide hydrochloride, it yields a compound, $C_{14}H_{15}O_2N_3$, forming small needles which melt and decompose at 262–264°; this is under investigation. With phenylhydrazine, the

triketone yields a red oil which crystallises with difficulty ; it has the composition $C_{19}H_{18}ON_2$, and melts at $87-88^\circ$. C. H. B.

Derivatives of *o*-Benzoquinone. By C. LORING JACKSON and WALDEMAR KOCH (*Amer. Chem. J.*, 1901, 26, 10-46).—When the lead salt of quinol is treated with an alcoholic solution of iodine, quinone is produced. Similarly, if the lead salt of catechol is shaken with a solution of iodine in chloroform, a garnet-red solution of *o*-quinone is obtained, which possesses no odour except that of the chloroform. If this solution is left for 24-30 hours, the *o*-quinone is completely converted into *o*-dihydroxyphenylhydroxy-*o*-quinone, which separates as a black precipitate ; all attempts to isolate *o*-quinone from the solution resulted in the formation of the same substance.

o-Dihydroxyphenylhydroxy-*o*-quinone, $C_6H_3(OH)_2 \cdot C_6H_2O_2 \cdot OH$, forms a nearly black, amorphous powder, which does not melt but decomposes gradually above 170° , and is readily soluble in alcohol, ether, or glacial acetic acid ; it yields a black, *lead* salt. This compound has also been obtained by Torrey and one of the authors by the electrolytic oxidation of catechol. On reduction with sodium amalgam, a black substance is formed, but catechol is not produced. The *tribenzoyl* derivative is obtained as a light yellow, amorphous powder, which is readily soluble in chloroform. By the action of phenylhydrazine on *o*-dihydroxyphenylhydroxy-*o*-quinone, a golden-yellow substance is produced containing 6.39 per cent. of nitrogen, whilst by the action of the same reagent on the tribenzoyl derivative, a substance containing 4.42 per cent. of nitrogen is obtained.

When dry hydrogen chloride is passed into a freshly prepared chloroform solution of *o*-quinone, *chlorocatechol*, $C_6H_3Cl(OH)_2$, is produced, which crystallises in white, pearly plates, and is readily soluble in water, alcohol, ether, benzene, chloroform, or acetone ; its *lead* salt was prepared and analysed. When the solution of *o*-quinone is treated with ammonium sulphide or sulphur dioxide, catechol is produced, whilst by the action of bromine tetrabromocatechol is formed. If the *o*-quinone solution is added drop by drop to a solution of benzenesulphinic acid in chloroform, *o*-dihydroxydiphenylsulphone, $SO_2Ph \cdot C_6H_3(OH)_2$, is produced, which crystallises in short, thick, white prisms, melts at 153° , dissolves readily in alcohol, ether, chloroform, or glacial acetic acid, and is apparently not identical with the compound obtained by Hinsberg and Himmelschein (*Abstr.*, 1896, i, 685) by the oxidation of catechol in presence of benzenesulphinic acid. By the action of aniline on the chloroform solution of *o*-quinone, dianilinoquinoneanilide is formed, identical with the compound prepared by Zincke and Hagen (*Abstr.*, 1885, 787) by the action of aniline and glacial acetic acid on *p*-quinone. When the solution of *o*-quinone is treated with *o*-phenylenediamine, a phenazine is not produced, but the diamine suffers oxidation.

When tetrabromo-*o*-quinone is heated with acetic acid, it is partially converted into *hexabromo-*o*-quinocatechol ether*, $C_{12}O_4Br_6$, which is obtained as a red precipitate, does not melt, and is soluble in all the common solvents ; it crystallises from warm nitrobenzene in short, slender, vermilion-red prisms, but undergoes decomposition if the solu-

tion is heated above 100°. This substance is more readily prepared by heating a solution of tetrabromo-*o*-quinone and tetrabromocatechol in acetic acid; if ether or chloroform is used as the solvent, no reaction takes place (compare Zincke, Abstr., 1887, 808). On reduction with sodium amalgam in an atmosphere of carbon dioxide, a purplish-white product is obtained together with a small proportion of catechol; when the purplish-white substance is treated with nitric acid, hexabromo-*o*-quinocatechol ether is regenerated, and may be again reduced with sodium amalgam; by repeating these alternate oxidations and reductions, the compound may be completely converted into catechol. The purplish-white compound is probably *hexabromo-o dihydroxycatechol ether*, $C_{12}Br_6O_2(OH)_2$; it crystallises from nitrobenzene in small, chocolate-brown needles, and does not melt below 300°. Hexabromo-*o*-quinocatechol ether is not decomposed when boiled with strong sulphuric acid, but if heated with concentrated hydrochloric acid at 160—175° in a sealed tube, it is converted into the purplish-white compound described above.

When tetrabromo-*o*-quinone is heated with tetrabromoquinol, bromoanil and tetrabromocatechol are formed; tribromopyrogallol reacts with it in a similar manner, with production of tetrabromocatechol, hexabromo-*o*-quinocatechol ether, and its purplish-white reduction product. If tetrabromo-*o*-quinone and tribromoresorcinol are allowed to react in acetic acid solution, a pink precipitate of *ditribromo-m-hydroxyphenyldibromo-o-quinophenylene ether*, $C_6Br_2O_2[C_6Br_3(OH)_2]_2$, is formed, which crystallises from benzene in slender, lemon-yellow prisms with square ends, melts at 217°, and is soluble in ether, alcohol, or chloroform, but does not dissolve in sodium hydroxide.

When tetrabromo-*o*-quinone is heated with glacial acetic acid, a white substance, $C_{14}H_2O_2Br_8$, is produced, which may be separated from the hexabromo-*o* quinocatechol ether simultaneously formed by extraction with hot alcohol, in which the latter is insoluble; it crystallises from glacial acetic acid in small, rhombic plates with a pearly lustre, is easily soluble in ether, benzene, chloroform, acetone, or ethyl acetate, and is extremely stable.

Ethyl acetate reacts with tetrabromo-*o*-quinone, with formation of tetrabromocatechol and hexabromo-*o*-quinocatechol ether. E. G.

Thymoquinone and Thymoquinol in Wild Bergamot Oil. By I. W. BRANDEL and EDWARD KREMERS (*Pharm. Review*, 1901, 19, 200—203 and 244—246).—The oil of *Monarda fistulosa* contains, in addition to cymene, thymol, and *d*-limonene, small quantities of thymoquinone and thymoquinol; the dark colour of the oil, and the colour produced in both its phenolic and non-phenolic portions on keeping, are probably due to the production of the highly coloured thymoquinhydrone. W. A. D.

Electrolytic Reduction of *o*-Nitroanthraquinone to *o*-Aminoanthraquinone. By JOH. MÖLLER (*Zeit. Elektrochem.*, 1901, 7, 741—743).—A solution of *o*-nitroanthraquinone (1 gram) in alcohol (270 grams) and concentrated sulphuric acid (30 grams) served as cathode solution in a cell with a diaphragm and platinum electrodes,

The anode solution was dilute sulphuric acid, temperature 50° , and current density 0.001 ampere per sq. cm. The yield of *o*-aminoanthraquinone was 70 per cent. of the theoretical quantity. T. E.

Action of Benzaldehyde on Sodiomenthol. New Methods of preparing Benzylidenementhone. By CAMILLE MARTINE (*Compt. rend.*, 1901, 133, 41—43).—The action of benzaldehyde on sodiomenthol yields an oil boiling at $182\text{--}185^{\circ}$ under 10 mm. pressure, and when this is heated with alcoholic potash, it yields potassium benzoate, menthol, benzyl alcohol, and a liquid boiling at $195\text{--}196^{\circ}$ under 15 mm. pressure. The last, when treated with hydrobromic acid in presence of acetic acid, yields benzylidenementhone hydrobromide, which forms silky needles melting at 115° . When treated with sodium ethoxide, it is converted into benzylidenementhone, which has $[\alpha]_D + 22.8^{\circ}$ to $+24.3^{\circ}$. The benzylidenementhone obtained according to Wallach's method by the action of hydrogen chloride on menthone and benzaldehyde, has the same rotatory power whether the original menthone is dextro- or lævo-gyrate. Similarly, the action of benzaldehyde on either *d*- or *l*-sodiomenthone yields the same *d*-benzylidenementhone. There is, however, evidence that a *l*-benzylidenementhone is formed at the same time in both cases, with an equal but opposite rotatory power, but forming no hydrobromide and no crystallisable oxime. It is clear that sodiomenthol behaves like sodiborneol in contact with benzaldehyde. The by-products obtained by the action of alcoholic potash indicate that the reaction takes place in the manner suggested by Claisen (*Abstr.*, 1887, 574). C. H. B.

cycloCitral Semicarbazone. By R. SCHMIDT (*Ber.*, 1901, 34, 2451).—The fact that β -cyclocitral is quantitatively regenerated from its semicarbazone by acids (*Ber.*, 1900, 33, 3721) is remarkable, since with the semicarbazones of aliphatic and hydroaromatic aldehydes more complex decomposition usually occurs, although with those of ketones a good yield of the ketone is usually obtained.

W. A. D.

New Derivatives of Benzylcamphor and Benzylidenecamphor. By ALBIN HALLER and JULES MINGUIN (*Compt. rend.*, 1901, 133, 79—84. Compare *Abstr.*, 1900, i, 452).—*Phenylbromohomocampholic acid*, $\text{CHPhBr}\cdot\text{CH}_2\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\text{H}$, prepared by treating benzylidenecampholic acid (*loc. cit.*) with a solution of hydrogen bromide in glacial acetic acid, forms hard, white crystals melting at 135° , and when dissolved in toluene has $[\alpha]_D + 44.8^{\circ}$. When heated at 100° with a solution of hydrogen bromide in acetic acid, phenylhydroxyhomocampholic acid is formed; with alcoholic potash, it yields a mixture of the last-mentioned acid and benzylidenecampholic acid.

Benzylbromocamphor, $\text{C}_8\text{H}_{14}\text{C}(\text{CO})\text{Br}\cdot\text{CH}_2\text{Ph}$, prepared by heating a solution of benzylcamphor in carbon disulphide with bromine, crystallises in large prisms belonging to the orthorhombic system, melts at $94\text{--}95^{\circ}$, and has $[\alpha]_D + 61^{\circ}$ in alcoholic solution. With alcoholic potash, it yields benzylidenecamphor, and thus differs

markedly in its behaviour from the isomeric bromobenzylcamphor (*loc. cit.*). By the action of heat alone, hydrogen bromide is eliminated with the formation of benzylidenecamphor. Hydrobromic acid has no action at 100°; when reduced with zinc and hydrochloric acid, benzylcamphor is regenerated. A second stereoisomeric *benzylbromocamphor* is also produced in the bromination of benzylcamphor in the manner just described, and forms crystals which melt at 90—91°, and have, when dissolved in alcohol, $[\alpha]_D + 20^\circ$. Towards heat and alcoholic potash, it behaves in the same manner as its stereoisomeride.

When the viscous product obtained on brominating benzylcamphor with excess of bromine is boiled with alcoholic potash, a mixture of *o*- and *p*-bromobenzylidenecamphor is obtained, which is separated by fractional crystallisation from alcohol, in which the para-compound is the less soluble.

p-Bromobenzylidenecamphor, $C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{CH} \cdot C_6H_4Br \\ \text{CO} \end{smallmatrix}$, crystallises in orthorhombic prisms, melts at 129—130°, and, when dissolved in toluene, has $[\alpha]_D + 315^\circ$. The *ortho*-derivative crystallises in monoclinic prisms, melts at 105°, and, when dissolved in toluene, has $[\alpha]_D + 283^\circ$. On oxidation with potassium permanganate, they yield respectively *p*- and *o*-benzoic acid together with camphoric acid.

p-Bromophenylhydroxyhomocampholic acid,
 $C_6H_4Br \cdot CH(OH) \cdot CH_2 \cdot C_8H_{14} \cdot CO_2H$,
 prepared by treating *p*-bromobenzylidenecamphor with a saturated solution of hydrogen bromide in acetic acid, and then boiling the additive product thus formed with alcoholic potash or hydrogen bromide in acetic acid, forms crystals which melt at 100°, and, when dissolved in toluene, have $[\alpha]_D + 57^\circ 3'$.
 K. J. P. O.

Combination of Camphor with β -Hydroxy- α -naphthaldehyde.
 By ANDRÉ HELBRONNER (*Compt. rend.*, 1901, 133, 43—45).—The action of the β -ethoxy- α -naphthaldehyde on sodiocamphor in presence of

toluene yields *ethoxynaphthylidenecamphor*, $OEt \cdot C_{10}H_6 \cdot CH : C \begin{smallmatrix} \text{CO} \\ \text{C}_8H_{14} \end{smallmatrix}$, which separates from alcohol in brilliant, white, highly refractive crystals of the hexagonal system. It melts at 100°, and has $[\alpha]_D + 121 \cdot 13^\circ$ in a 5.32 per cent. alcoholic solution. With sulphuric acid, it gives a blood red coloration, which disappears if water is added. With sodium amalgam, it yields the corresponding hydro-derivative,

$OEt \cdot C_{10}H_6 \cdot CH_2 \cdot CH \begin{smallmatrix} \text{CO} \\ \text{C}_8H_{14} \end{smallmatrix}$, which melts at 112°, and has $[\alpha]_D + 52 \cdot 8^\circ$.
 The analogous *methoxynaphthylidenecamphor* crystallises in hexagonal forms, melts at 78°, and has $[\alpha]_D + 119 \cdot 86^\circ$, whilst its reduction product melts at 96° and has $[\alpha]_D 57 \cdot 8^\circ$.
 C. H. B.

Phellandrene Nitrite and Oils containing Phellandrene. By OSWALD SCHREINER (*Pharm. Arch.*, 1901, 4, 90—95).—Crude phellandrene nitrite, prepared from a eucalyptus oil containing phellandrene, has $[\alpha]_D + 28 \cdot 5^\circ$, but can be resolved by fractional crystallisation from ethyl acetate and methyl alcohol into two components of different optical activity. One of these melts at 120—121°, has $[\alpha]_D + 123 \cdot 5^\circ$,

and forms long, well-defined needles, whilst the other melts at 100—101°, has $[\alpha]_D -36^\circ$, and crystallises in confused aggregates. The melting point of the latter changes to 105—106° on crystallisation from methyl alcohol, so that evidently it does not correspond with a definite compound. The highest melting point hitherto given for phellandrene nitrite is 105° (Wallach and Herbig, *Abstr.*, 1896, i, 101), the pure substance probably never having been obtained; as a consequence, all previous diagnoses of the presence of phellandrene in many ethereal oils, based on the formation of a nitrite melting at about 105°, are inexact.

W. A. D.

Conversion of Thujiylamine into Thujene. By L. TSCHUGAEFF (*Ber.*, 1901, 34, 2276—2281).—The dry distillation of thujiylamine hydrochloride gives *isothujene* and not *thujene*, which might have been expected as the first product of the action. *Trimethylthujiylammonium iodide*, $C_{10}H_{17}Me_3NI$, prepared by the action of methyl iodide and potassium hydroxide on thujiylamine, crystallises from a mixture of chloroform and methyl alcohol in long, prismatic crystals, has $[\alpha]_D +42.61^\circ$ in chloroform solution, and is only sparingly soluble in cold water. The *base*, $C_{10}H_{17}Me_3N \cdot OH$, mixed with carbonate, was obtained as a crystalline mass, and was decomposed by dry distillation. The product consisted of thujene, which boils at 151—153°, has a sp. gr. 0.8263 at 20°/4°, $n_D 1.45022$ at 20°, and $[\alpha]_D -8.23^\circ$; these constants are entirely different from those of Wallach's *isothujene*, but agree closely with those of the thujene prepared from thujiyl alcohol through the xanthate (this vol., i, 38). The rotatory power is, however, nearly twice as great as that of the thujene from thujiyl alcohol, and it is suggested that two stereoisomeric alcohols are perhaps formed by the reduction of thujone, and that these give rise to two stereoisomeric thujenes; by collecting the last fraction in the distillation of methyl thujiylxanthate, a dextrorotatory thujene was obtained which has $\alpha_D +21.83^\circ$ in a 10 cm. tube. *Dimethylthujiylamine*, $C_{10}H_{17}NMe_2$, formed as a by-product in the preparation of trimethylthujiylamine iodide, is a liquid boiling at 213.5—214°, has a sp. gr. 0.8606 at 20°/4°, and $[\alpha]_D +141.76^\circ$; the *hydrochloride* is very readily soluble in water and alcohol, but the *nitrate* is only sparingly so and crystallises readily; the *platinichloride* separates from hot alcohol as an orange-red, crystalline powder.

T. M. L.

Oil of Jasmine-blossoms. By ERNST ERDMANN (*Ber.*, 1901, 34, 2281—2283. Compare Hesse, *Abstr.*, 1900, i, 454; this vol., i, 220).—In reply to Hesse, it is urged that it is very unlikely that large amounts of scent are produced during enfleurage, and the difference in yield by enfleurage and by extraction with light petroleum is explained as due merely to a difference in conditions.

T. M. L.

Oil of Neroli. By ERNST ERDMANN and HUGO ERDMANN (*Ber.*, 1901, 34, 2283).—A question of priority (compare Walbaum, this vol., i, 39).

T. M. L.

Formation of Resin in several Abietes. By ALEXANDER TSCHIRCH and E. FABER (*Arch. Pharm.*, 1901, 239, 249—257).—The

authors discuss the question of the origin of resin and the part played by the bark in its formation.
K. J. P. O.

Robinin and Rutin. By ERNST SCHMIDT (*Chem. Centr.*, 1901, ii, 121; from *Apoth.-Zeit.*, 16, 357—358. Compare Perkin, *Proc.*, 1901, 17, 87—88).—By the decomposition of robinin, rhamnose and a yellow dye are formed. The latter, $C_{15}H_{10}O_6$, crystallises from hot water in slender needles, and is very similar to Tschirch and Polacco's rhamnolutin. It is easily attacked by dilute potassium hydroxide solution, and forms an acetyl derivative, $C_{15}H_6O_2(OAc)_4$, which separates in colourless crystals and melts at 182—183°. The ethyl derivative crystallises in yellow needles. The mother liquor of robinin contains asparagine and sugar.

[With WALJASCHKO.]—Rutin, prepared from *Ruta graveolens*, when hydrolysed, forms rhamnose, dextrose, and quercetin, the last being identical with that prepared from quercitrin. The rutin obtained from common rue is not identical with robinin or quercetin, but resembles the rutin isolated from capers, and also that from *Viola tricolor* (Mandelin and Wachs).
E. W. W.

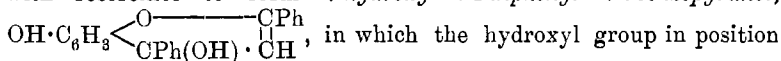
Uganda Aloes. By ALEXANDER TSCHIRCH and J. KLAIVENESS (*Arch. Pharm.*, 1901, 239, 241—257. Compare this vol. i, 399).—Uganda aloes, on distillation with 1 per cent. potassium carbonate solution, yield a small quantity of an ethereal oil which has an odour of roses and solidifies. By Léger's method (*Bull. Soc. Chim.*, 1900, [iii], 23, 790), *uganda-aloin*, $OMe \cdot C_{15}H_{11}O_4(OH)_2$, was obtained, and is identical with capaloin (m. p. 138—139°) prepared from Cape aloes by Léger (*loc. cit.*). The *dibenzoyl* derivative forms a pale yellow powder melting at 107—108°. With chlorine and bromine, *uganda-aloin* gives crystalline compounds, and with hydrochloric acid a black powder (*alonigrin*). On oxidation with nitric acid, chrysaminic, picric, and oxalic acids are produced.

The resin from Uganda aloes consists of *uganda-aloresinotannol p-coumarate*, which is identical with or nearly related to the ester found in Natal aloes. Emodin is also present, and can be isolated by extracting Uganda aloes with acetone, and precipitating the resin with ether, or by extracting with ether the acid mother liquor from the preparation of the resin.
K. J. P. O.

Later Developments of the Chemistry of the Anthracene Dyes. By A. BUNTROCK (*Ber.*, 1901, 34, 2344—2349).—A reply to and criticism of papers by Liebermann (see this vol. i, 478).
R. H. P.

Bilirubin, the Red Colouring Matter of the Bile. By WILLIAM R. ORNDORFF and J. E. TEEPLE (*Amer. Chem. J.*, 1901, 26, 86—92).—The average of a large number of analyses of bilirubin, obtained from ox gall-stones and crystallised from dimethylaniline, indicates the formula $C_{34}H_{36}O_7N_4$; it contains no alkyloxy-groups, but has one alkyl group attached to nitrogen, and is probably a pyrrole derivative.
E. G.

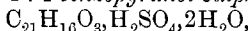
Derivatives of 1:4-Benzopyranol, the Parent Substance of a New Class of Colouring Matters. III. By CARL BÜLOW and WALTHER VON SICHERER (*Ber.*, 1901, **34**, 2368—2385. Compare this vol., i, 400, 559).—The 1:3-diketone, dibenzoylmethane, condenses with resorcinol to form 7-hydroxy-2:4-diphenyl-1:4-benzopyranol,



in which the hydroxyl group in position 4 remains intact (compare *loc. cit.*) and exhibits carbinolic rather than phenolic properties. The *hydrochloride*, $\text{C}_{21}\text{H}_{16}\text{O}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$, is obtained by the condensation of resorcinol with dibenzoylmethane in acetic acid solution in the presence of hydrogen chloride, and crystallises in large, yellowish-orange or orange needles, which begin to decompose about 200° and give an intense yellow-green fluorescence when dissolved in sulphuric acid. The colour *base* crystallises in ruby-red needles decomposing at $250\text{--}260^\circ$.

When the hydrochloride is distilled with 10 per cent. potassium hydroxide, acetophenone passes over and benzo-resorcinol is found in the alkaline liquor together with a small quantity of benzoic acid, arising from the decomposition of the last-mentioned substance.

7-Hydroxy-2:4-diphenyl-1:4-benzopyranol sulphate,



prepared from the hydrochloride and alcoholic sulphuric acid, crystallises in orange-red needles; the *picrate* forms yellow needles darkening at 200° and decomposing at 260° ; the *platinichloride*, lemon-yellow, insoluble needles decomposing suddenly at 235° ; the *aurichloride*, canary-yellow plates melting and decomposing at 236° .

The *diacetyl* derivative of the benzopyranol, prepared from the hydrochloride and acetic anhydride, crystallises in red needles melting and decomposing at $110\text{--}112^\circ$, fluoresces with concentrated sulphuric acid, and is insoluble in alkalis. The *monoacetyl* derivative is formed when the diacetyl compound is heated with boiling dilute sulphuric acid, and crystallises in red needles melting at 119° , and easily soluble in alkalis; the monoacetyl compound is readily benzoylated by the Schotten-Baumann method.

The *dibenzoyl* derivative, prepared from the hydrochloride, forms ruby-red, prismatic crystals decomposing slowly at 110° .

The *dimethyl ether*, prepared from methyl iodide and the sodium derivative of the benzopyranol, crystallises in white needles melting at 104° and dissolves in concentrated sulphuric acid, forming a colourless solution which exhibits a fine yellowish-green fluorescence.

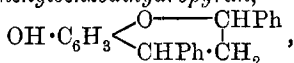
2:3-Dibromo-7-hydroxy-2:4-diphenyl-1:4-benzopyranol, $\text{C}_{21}\text{H}_{16}\text{O}_3\text{Br}_2$, prepared by the action of bromine on an acetic acid solution of the hydrochloride, is an additive compound crystallising in reddish-brown spikes, decomposing at 240° , and easily soluble in dilute alkalis; its solution in sulphuric acid is not fluorescent; by zinc dust and acetic acid, it is converted into a colourless substance which does not contain bromine.

8-Nitroso-7-hydroxy-2:4-diphenyl-1:4-benzopyranol, $\text{C}_{21}\text{H}_{15}\text{O}_3 \cdot \text{NO}$, crystallises in scarlet needles softening at 135° and melting at 158° .

By the action of hydrochloric acid under pressure on the hydrochloride, a *substance*, $\text{C}_{21}\text{H}_{15}\text{O}_2\text{Cl} \cdot \text{HCl}$, is obtained which crystallises in

yellow spikes, decomposing slowly at 140—170°, and losing hydrogen chloride on exposure to air. The authors regard this substance as the hydrochloride of a chloro-derivative of the benzopyranol, in which chlorine has replaced the carbinolic hydroxyl.

7-Hydroxy-2 : 4-diphenylbenzodihydropyran,



prepared by long boiling of the acetic acid solution of the hydrochloride of the benzopyranol with zinc dust, forms a white, amorphous powder, which becomes red at 142° and above 150° decomposes; it dissolves in alkalis, does not fluoresce with sulphuric acid, and is oxidised to the benzopyranol by mercuric oxide, &c.

If in the reduction the boiling is stopped as soon as the solution becomes colourless, the liquid contains a substance, which oxidises most readily in the air, and is probably the leuco-base, the carbinolic hydroxyl group having been replaced by hydrogen. The *acetyl* derivative of the benzodihydropyran, $\text{C}_{21}\text{H}_{17}\text{O}_2\text{Ac}$, forms a yellowish, amorphous powder melting at 112—115°. K. J. P. O.

Dinaphthoxanthenes. By R. FOSSE (*Compt. rend.*, 1901, 133, 100—102).—*Bromodinaphthoxanthone*, $\text{CHBr} \left\langle \begin{array}{c} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{array} \right\rangle \text{O}$, prepared by the action of bromine on a solution of dinaphthoxanthone in bromoform, crystallises in red prisms (green by reflected light) and melts at 218—220°. It is soluble in moderately diluted, but not in concentrated acids. From the solution in hydrobromic acid, a hydrated hydrobromide crystallises in golden-red needles. With alcohol, this bromo-derivative reacts, yielding aldehyde, hydrogen bromide, and dinaphthoxanthone.

Bisdinaphthoxanthoneamine, $\text{NH} \cdot [\text{CH} : (\text{C}_{10}\text{H}_6)_2 : \text{O}]_2$, prepared from the bromo-derivative and alcoholic or aqueous ammonia, forms lustrous crystals melting and decomposing at 230°. With hydrobromic acid, the amine becomes blood-red and decomposes into ammonium bromide and bromodinaphthoxanthone; with hydrochloric acid, into ammonium chloride and chlorodinaphthoxanthone.

Chlorodinaphthoxanthone, $\text{CHCl} : (\text{C}_{10}\text{H}_6)_2 : \text{O}$, prepared by the action of chlorine on dinaphthoxanthone, crystallises in red needles melting at 150°. It resembles the bromo-derivative in properties, and forms compounds with mercuric chloride or bromide and with platonic chloride. K. J. P. O.

Action of Vegetable Alkaloids on certain Indicators. By A. ASTRUC (*Compt. rend.*, 1901, 133, 98—100).—Solutions of various alkaloids in water, absolute alcohol, amyl alcohol, or benzene were titrated with hydrochloric acid in the presence of the indicators helianthin A, rosolic acid, and phenolphthalein.

Of the alkaloids derived from pyridine, those containing a piperidine nucleus are stronger bases than those containing only the unreduced pyridine nucleus. Thus, conicine, conhydrine, and sparteine act on the three indicators in aqueous solution, whilst nicotine and pilocarpine (alkaloids derived from pyridine) do not affect phenolphthalein; in a neutral medium, the former have an action on helianthin A and rosolic

acid, the latter only on helianthin A. Sparteine possesses two basicities; in aqueous solution, in the presence of helianthin A, it requires 2 mols. of hydrogen chloride, but in the presence of rosolic acid or phenolphthalein, it requires only 1 mol. of the acid for neutralisation. Further, in a neutral solvent, sparteine behaves as a univalent base towards rosolic acid. These facts show that sparteine possesses one piperidine and no pyridine nucleus.

Of the alkaloids derived from trapanine, trapanine, atropine, and hyoscyamine in aqueous solution are strong bases, and behave towards indicators as does piperidine. In benzene solution, trapanine is basic towards rosolic acid, whilst atropine and hyoscyamine are neutral. Ecgonine and benzoylecgonine are without action on indicators in aqueous solution; in benzene, they are neutral to rosolic acid, univalent bases in presence of helianthin A, and univalent acids in presence of phenolphthalein.

The alkaloids derived from quinoline (quinine, cinchonine, cinchonidine, &c.) have two basicities; in aqueous solution, they are neutral to phenolphthalein, require 1 mol. of hydrogen chloride in presence of rosolic acid, and 2 mols. in presence of helianthin A. In benzene, quinine acts only on the last-mentioned indicator, and is bivalent.

Of the alkaloids derived from oxazine and isoquinoline (in which class are included the alkaloids from opium) codeine, morphine, and thebaine, when dissolved in water or dilute alcohol, can be approximately titrated in the presence of rosolic acid, whilst papaverine, narceine, and narcotine are neutral to this indicator; all are univalent bases towards helianthin A. In benzene solution, they all affect the last-mentioned indicator; morphine and narceine in this solvent can respectively be titrated approximately by potassium hydroxide in the presence of phenolphthalein.

Aconitine, veratrine, strychnine, and brucine only act as feeble bases on helianthin A.

Of the purine group of bases, hydrated caffeine is neutral to all indicators; a solution of the anhydrous base in benzene affects methyl-orange, but cannot be titrated in the presence of this indicator.

It is pointed out that there is a complete parallelism between the thermochemistry of these bases and their behaviour towards indicators.

K. J. P. O.

Relation of Hyoscyamine to Atropine and of Scopolamine to *i*-Scopolamine. By JOHANNES GADAMER (*Arch. Pharm.*, 1901, 239, 294—336. Compare *Abstr.*, 1900, i, 91).—By the action of water at the ordinary temperature, hyoscyamine is hydrolysed to *l*-tropic acid and *i*-tropine, whilst by alkalis this base is converted into atropine (*i*-tropine *r*-tropate), and at the same time partially hydrolysed. The change of hyoscyamine into atropine then is a conversion of *l*-vortatory tropic acid into racemoid tropic acid. Addition of tropine to an aqueous solution of hyoscyamine hastens the hydrolysis, and, at the same time, effects a certain amount of conversion into atropine, which in its turn is to a small extent hydrolysed. In alcoholic solution, hyoscyamine is slowly transformed into atropine, a change which is hastened by addition of tropine.

The conversion of hyoscyamine into atropine is best effected as follows. A solution of the base (1 gram) in absolute alcohol (15 grams), to which sodium hydroxide (0.03 gram) has been added, is allowed to remain at 5° until it is inactive (about 24 hours). Carbon dioxide is passed in, the filtered solution evaporated under reduced pressure, and water added to precipitate the atropine.

Scopolamine (*i*-scopoline *l*-tropate) in a similar manner is converted by alkalis into *i*-scopolamine (that is, Hesse's atropine, *i*-scopoline *r*-tropate) and also partially hydrolysed into scopoline and *l*-tropic acid. In absolute alcohol, no change takes place until tropine is added.

The existence of these changes explains the fact that in young roots of *Belladonna* only hyoscyamine is present, whilst in old roots atropine is found as well.

The author finds that scopolamine in alcoholic solution has $[\alpha]_D - 18^\circ$ at 20° and in aqueous solution -28° ; the hydrobromide has $[\alpha]_D - 15.72^\circ$ in alcoholic solution. Pure *l*-tropic acid, prepared by hydrolysis of scopolamine in aqueous solution, crystallises from water in needles melting at 125—126°, and has $[\alpha]_D - 71.81^\circ$. Alkalis have no effect on the rotation of the pure acid.

Inactive atropine, prepared in a completely pure state by the method previously described, melts at 115—116°, and when pulverised at 112—113°. The sulphate, when carefully dried over sulphuric acid, melts at 187—188°, but traces of moisture greatly depress the melting point. The author believes that the surest means of testing atropine sulphate for the presence of hyoscyamine is by use of the polarimeter.

K. J. P. O.

Stereochemistry of the Piperidine Series. II. By W. HOHENEMSER and RICHARD WOLFFENSTEIN (*Ber.*, 1901, 34, 2420—2423. Compare *Abstr.*, 1899, i, 936).—The same laws connecting structure and specific rotatory power as were established in the former paper hold for the following alkyl derivatives of coniine; these bases were prepared by heating coniine with solid potassium hydroxide and a slight excess of the alkyl bromide for 14 hours at 170°. 1-*Ethylconiine* boils at 187—188° under 755 mm. pressure, and has a sp. gr. 0.8398 at 21°, $[\alpha]_D 75.62^\circ$ and $[M]_D 117.21$; the *hydrochloride* melts at 111°, the *hydrobromide* at 163°, the *platinichloride* at 110—111°, the *aurichloride* at 85—86°, whilst the *mercurichloride* and *picrate* are oils. 1-*Propylconiine* boils at 207—208° under 764.3 mm. pressure, and has a sp. gr. 0.8423 at 18°, $[\alpha]_D 76.21^\circ$, $[M]_D 128.80$; the *hydrochloride* melts at 144°, the *hydrobromide* at 186°, the *platinichloride* at 172—173°, the *aurichloride* at 103—104°, and the *picrate* at 60°; the *mercurichloride* is an oil.

1-*isoAmylconiine* boils at 238—240° under 773.4 mm. pressure, and has a sp. gr. 0.8352 at 23.5°, $[\alpha]_D 75.14^\circ$, $[M]_D 148.02$; the *hydrochloride* is deliquescent, the *hydrobromide* melts at 132.5°, the *aurichloride* at 97—98°, and the *picrate* at 66.5°; the *platinichloride* and *mercurichloride* are oils.

The foregoing active bases could not be purified by conversion into the *d*-tartrates, owing to these salts not crystallising well; the rotatory powers given apply to bases which were isolated directly, and are most

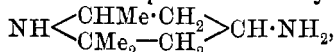
probably correct, since on heating these substances with solid potassium hydroxide for 14 hours at 170° , no change of rotatory power occurs.

W. A. D.

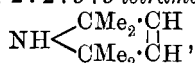
New Alkaloid from the Elder Tree. By F. MALMÉJAC (*J Pharm.*, 1901, [vi], 14, 17—19).—See this vol., ii, 572.

Aminopyrrolidines. By HERMANN PAULY and A. SCHAUM (*Ber.*, 1901, 34, 2287—2289. Compare Pauly and Rossbach, *Abstr.*, 1899, i, 773, and Pauly and Boehm, *Abstr.*, 1900, i, 357).—3-Amino-

2:2:5:5-tetramethylpyrrolidine, $\text{NH} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CH}_2 \\ \text{CMe}_2 \cdot \text{CH} \cdot \text{NH}_2 \end{smallmatrix}$, very closely resembles the two stereoisomeric *p*-aminotrimethylpiperidines,



of Harries (*Abstr.*, 1896, i, 317), but differs from them in that nitrous acid does not convert it into the corresponding hydroxy-compound, but gives the unsaturated 2:2:5:5-tetramethylpyrroline,

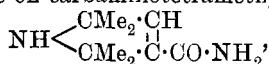


which is a mobile liquid and boils at 114 — 116° . It also resembles Harries' α -compound in that it gives two isomeric *thiocarbamates* melting at 142 — 144° and 170° respectively. The 1-methyl derivative,

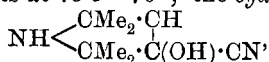
$\text{NMe} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CH}_2 \\ \text{CMe}_2 \cdot \text{CH} \cdot \text{NH}_2 \end{smallmatrix}$, is an ice-like mass which melts at 40° , boils at 190° , and also gives two *thiocarbamates* melting at 103° and 172° respectively.

T. M. L.

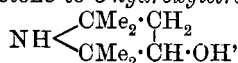
3-Keto-2:2:5:5-tetramethylpyrrolidine. By HERMANN PAULY and CARL BOEHM (*Ber.*, 1901, 34, 2289—2291).—3-Keto-2:2:5:5-tetramethylpyrrolidine, $\text{NH} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CH}_2 \\ \text{CMe}_2 \cdot \text{CO} \end{smallmatrix}$, prepared by the action of potassium hypobromite on carbaminotetramethylpyrroline,



is a mobile liquid readily volatile in a current of steam; it boils at 175° , and as a ketonic secondary amine very closely resembles triacetoneamine. The *nitrosoamine*, $\text{NO} \cdot \text{N} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CH}_2 \\ \text{CMe}_2 \cdot \text{CO} \end{smallmatrix}$, forms yellow felted needles, and melts at 75.5 — 76° ; the *cyanohydrin*,



forms minute tablets, melts at 138° , and is readily decomposed; the *oxime* crystallises in tablets or prisms, melts at 172° and is reduced by sodium and alcohol to 3-aminotetramethylpyrrolidine. Sodium amalgam reduces the ketone to 3-hydroxytetramethylpyrrolidine,



which forms square tablets, melts at 71° , and boils at 90 — 91° under 11.5 mm. pressure; a *base*, $\text{C}_8\text{H}_{19}\text{ON}$, is also produced by further

reduction; it crystallises in prisms, melts at 26° , boils at $87.8-88^{\circ}$ under 11.5 mm. pressure, and is separated from the preceding compound by means of the difference in solubility of the hydrochlorides in acetone. The *benzoate* of *p*-hydroxytetramethylpyrrolidine is a powerful local anæsthetic. T. M. L.

Stereochemistry in the Piperidine Series. II. By ARTHUR MARCUSE and RICHARD WOLFFENSTEIN (*Ber.*, 1901, 34, 2426—2430).—Lupetidine and *isolupetidine* (2:6-dimethylpiperidines; Abstr., 1899, i, 937), differ notably in their behaviour with acid chlorides; with benzenesulphonic chloride, the former interacts only slowly and under special conditions, whilst the latter acts rapidly and completely, although with benzoyl chloride the converse is true. With phenylcarbimide and phenylthiocarbimide, however, the action of the two bases is the same. That the difference of action is due to the different influences on the imino-group of the two adjacent methyl radicles occupying respectively a *cis*- and *trans*-position, is shown by the fact that the two isomeric forms of copellidine (2-methyl-5-ethylpiperidine) interact with all the foregoing substances with equal ease.

Lupetidine does not combine with benzenesulphonic chloride in presence of aqueous sodium hydroxide, but with potassium hydroxide yields a small quantity of the *derivative*, $C_{13}H_{19}O_2NS$, melting at 50° . In presence of either sodium or potassium hydroxide, *isolupetidine* readily yields large quantities of the isomeric compound melting at 65° . The *benzoyl* derivative of lupetidine melts at 111° , that of *isolupetidine* at 84° . The phenylcarbimide *derivative* of lupetidine melts at 147° , the solubility in benzene at 15° being 0.86 per cent.; the analogous *isolupetidine* derivative melts at 102° , the solubility being 12.6 per cent. The analogous phenylthiocarbimide *derivatives* of lupetidine and *isolupetidine* melt at $83-84^{\circ}$ and $112-113^{\circ}$ respectively.

The benzenesulphonic *derivative* of copellidine is an oil, the analogous *isocopellidine* derivative melts at 66° ; the analogous *benzoyl* derivatives are both oils. The phenylcarbimide *derivative* of copellidine melts at $97-98^{\circ}$, and of *isocopellidine* at $232-233^{\circ}$. W. A. D.

Hydrogen Peroxide. By ARTHUR MARCUSE and RICHARD WOLFFENSTEIN (*Ber.*, 1901, 34, 2430—2432).—Lupetidine combines with concentrated aqueous hydrogen peroxide to form the *salt*, $2C_7H_{15}N, H_2O_2$, which crystallises from ether and melts at $69-70^{\circ}$, the existence of this salt proving the essentially acid nature of hydrogen peroxide. Solutions of the latter, moreover, give an acid reaction, which disappears when the hydrogen peroxide is destroyed by spongy platinum, the solution becoming neutral. W. A. D.

Conversion of Ammonia Derivatives into Ammonium Hydroxides in Aqueous Solutions. By GEORG BREDIG (*Zeit. Elektrochem.*, 1901, 7, 767—768).—The index of absorption for electrical oscillations of a mixture of equal volumes of pyridine and water is 0.036, that of pyridine alone is 0.018, whilst water alone has a very small absorption. From the conductivity of the mixture an index of absorption 0.005 is calculated.

A 66 per cent. solution of betaine has the index of absorption 0.182, the value calculated from its conductivity being 0.0011. Since Drude

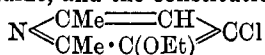
has shown that a very large index of absorption for electrical oscillations is characteristic of hydroxyl compounds, these results point to the formation of compounds of pyridine and betaine with water.

T. E.

Nitrogenous Bases in Roumanian Petroleum. By ARTHUR B. GRIFFITHS and N. J. BLUMAN (*Bull. Soc. Chim.*, 1901, [iii], 25, 725—726).—The crude petroleum of sp. gr. 0.8445 at 15° was agitated with dilute sulphuric acid and the solution rendered alkaline and extracted with ether; a dark brown, thick, oily liquid boiling at 117° was obtained, which had the composition of pyridine, but differed from this base by being insoluble in water. On reduction, it yielded piperidine, and probably, therefore, was a hydropyridine.

W. A. D.

Action of Phosphorus Oxychloride on Ethyl Aminocrotonate. By AUGUST MICHAELIS and K. VON AREND (*Ber.*, 1901, 34, 2283—2287).—*Chloroethylutidine*, $C_9H_{12}ONCl$, prepared by the action of phosphorus oxychloride on ethyl aminocrotonate, is an oil, with a slight odour of pepper, which boils at 132° under 12 mm. pressure, and at 257—260° with slight decomposition under atmospheric pressure, is readily soluble in all organic solvents, but only slightly so in water, has a sp. gr. 1.155 at 17°/17°, n_D 1.5098 at 17°, and a normal molecular weight in freezing benzene. The *hydrochloride*, $C_9H_{12}ONCl \cdot HCl$, is a white, crystalline substance which melts at about 134° and dissolves readily in alcohol or water, but not in ether. The *mercurichloride*, $C_9H_{12}ONCl \cdot HCl \cdot HgCl_2$, forms white crystals and melts at 112—113°. The *platinichloride*, $(C_9H_{12}ONCl)_2 \cdot H_2PtCl_6 \cdot 4H_2O$, forms red crystals, dissolves readily in hot water or alcohol, and melts at 196—198°. The *aurichloride* is an oil which gradually crystallises. The base is converted into lutidine by passing the vapour over heated zinc dust; when boiled with concentrated hydrochloric acid, it loses ethyl chloride and is converted into a crystalline phenolic compound; potassium hydroxide gives a compound $C_9H_{12}O_2NK$, in which the chlorine atom is displaced by the radicle OK. The base is, therefore, regarded as a derivative of 2:6-lutidine, and the constitution



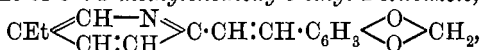
is provisionally assigned to it.

T. M. L.

Action of Aldehydocollidine [2-Methyl-5-ethylpyridine] on Substituted Aromatic Aldehydes. *Phenyl- α -picolylalkine* [*2- β -Hydroxy- β -phenylethylpyridine*]. By HERMANN BACH (*Ber.*, 1901, 34, 2223—2237).—2-Methylpyridine reacts with aldehydes in two ways, condensation with elimination of water, and formation of a stilbazole taking place at a high temperature in absence of water, and aldol condensation, with formation of a picolylalkine, occurring at a lower temperature in presence of water. The course of the reaction, however, also depends on the nature of the aldehyde, and the following experiments show that the meta-aldehydes react almost entirely to form stilbazoles, whilst the ortho-aldehydes almost exclusively produce

alkines. With the para-aldehydes, the difference is not so marked, but the yield of alkine is much greater than that of stilbazole.

2-Methyl-5-ethylpyridine reacts with piperonal at 230—250° to form a small amount of 3':4'-methylenedioxy-5-ethyl-2-stilbazole,



which crystallises in colourless, silky needles melting at 92°. The *hydrochloride* decomposes at 204°, the *mercurichloride* crystallises in needles melting at 200°, and the *platinichloride* melts and decomposes at 192°. Only a trace of the corresponding alkine could be obtained.

3'-Nitro-5-ethyl-2-stilbazole, $\text{CEt} \begin{array}{c} \text{CH}-\text{N} \\ \diagup \quad \diagdown \\ \text{CH}:\text{CH} \end{array} \text{C} \cdot \text{CH}:\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, is readily obtained from 2-methyl-5-ethylpyridine, the yield being 85 per cent. of the theoretical; it crystallises in lustrous plates melting at 66°. The *hydrochloride* crystallises in silky needles melting at 194°, the *platinichloride* melts at 178°, and the *aurichloride* at 176°. The *hydrobromide* decomposes at 135°, the *dichromate* melts at 103—104°, and the *picrate* at 220°. No trace of the corresponding alkine could be obtained. Since Castner (this vol., i, 562) and Roth (this vol., i, 165) have shown that *o*-nitrobenzaldehyde gives good yields of alkine, but very small yields of stilbazole, with 2-methyl-5-ethylpyridine and 2-picoline, this points to a marked difference of behaviour between the isomeric aldehydes.

4'-Nitro-5-ethyl-2-stilbazole, $\text{C}_5\text{NH}_3\text{Et} \cdot \text{CH}:\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, is formed to the extent of about 20 per cent. of the theoretical amount from *p*-nitrobenzaldehyde and 2-methyl-5-ethylpyridine at 160°, and crystallises in lustrous, light yellow plates melting at 116°. The *hydrochloride* crystallises in slender needles, and melts and decomposes at 112°; the *mercurichloride* melts at 188°, the *platinichloride* at 199—200°, and the *picrate* at 212°. The corresponding *p*-nitrophenyl-5-ethyl-2-methylpyridylalkine [2-β-hydroxy-β-*p*-nitrophenylethyl-5-ethylpyridine], $\text{C}_5\text{NH}_3\text{Et} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, is formed to the extent of 70 per cent. from *p*-nitrobenzaldehyde, 2-methyl-5-ethylpyridine, and water at 150°, and crystallises in colourless, silvery plates melting at 147°. The *hydrochloride* melts at 103°, the *mercurichloride* melts and decomposes at 175—180°, the *platinichloride* melts at 141°, and the *picrate* at 126°.

2-β-Hydroxy-β-phenylethylpyridine, $\text{C}_5\text{NH}_4 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH})\text{Ph}$, is converted by reduction into α-stilbazoline, which was previously obtained by Baurath (Abstr., 1888, 608) by the reduction of the corresponding α-stilbazole; it is also readily converted into the mononitro-derivative, which has been previously prepared synthetically by Roth. The stilbazole, on the other hand, does not give a nitro-derivative (Baurath).

Attempts to resolve 2-β-hydroxy-β-phenylethylpyridine into its optically active constituents by means of the *d*-tartrate failed, and the base is probably an instance of a partially racemic substance. The *hydrogen d-tartrate* crystallises with 2H₂O in very slender needles, and melts at 171°.

A. H.

Formation of *ana*-Nitroquinoline [5-Nitroquinoline] from *m*-Nitroaniline. By HERMAN DECKER (*J. pr. Chem.*, 1901, [ii], 63, 573—576).—By the action of glycerol, sulphuric acid, and nitrobenzene on *m*-nitroaniline, La Coste (Abstr., 1883, 811) prepared phenanthroline, whilst Claus and Stiebel (Abstr., 1888, 295), by the use of picric acid, obtained 10 per cent. of 3-nitroquinoline, together with phenanthroline. By the use of arsenic acid as oxidising agent, the author obtained a mixture of 20 per cent. of 3-nitroquinoline and 80 per cent. of 5-nitroquinoline. This compound melts at 72°; the *hydrochloride* forms quadratic plates melting and decomposing at 214°; the *ethiodide*, dark red prisms. On methylation and oxidation, it yields 5-nitromethylquinolone (m. p. 166°). K. J. P. O.

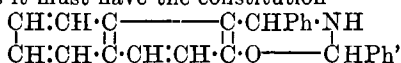
***o*-Toluquinaldine [2:8-Dimethylquinoline]. A Correction.** By ALEXANDER EIBNER (*Ber.*, 1901, 34, 2450).—The *picrate* of 2:8-dimethylquinoline crystallises from chloroform-alcohol in golden needles or prisms, and melts at 180°, not at 166°, as previously stated (*Ber.*, 1900, 33, 3467). W. A. D.

Constitution of *p*-Toluquinophthalone [*p*-Methylquinophthalone]. By ALEXANDER EIBNER and E. SIMON (*Ber.*, 1901, 34, 2303—2311. Compare this vol., i, 348).—*p*-Methylquinophthalone melts at 231—232° (not at 203° as given by Jacobson and Reimer, Abstr., 1884, 335); the *monobromo*-derivative crystallises in six-sided leaflets and melts at 159—160°; the *tribromo*-derivative, obtained by bromination in chloroform solution, crystallises in orange-yellow prisms, melts and decomposes at 233—234°, and in benzene solution decomposes into the crystalline *hydrobromide* of the phthalone; the *mononitro*-derivative crystallises in dark yellow prisms melting at 132°, and the *anil* in small, slender, felted, red needles melting at 233°.

The asymmetric constitution of *p*-methylquinophthalone is proved by the formation of two isomeric methylquinophthalines. *p*-Methyl-*α*-quinophthaline, $\text{NH}:\text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \end{array} \text{C}:\text{CH}\cdot\text{C}_9\text{NH}_5\text{Me}$, obtained by heating the phthalone with alcoholic ammonia at 200°, crystallises in red, felted needles, melts at 270—271°, and when heated with aniline gives the above described anil. *p*-Methyl-*β*-quinophthaline, obtained by heating *p*-toluquinaldine with phthalimide and zinc chloride, crystallises in lustrous, gold leaflets, and melts at 209°. R. H. P.

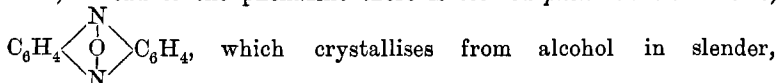
Condensation between *β*-Naphthol, Aldehydes, and Amines.
II. Synthesis of Oxazine Derivatives. By MARIO BETTI (*Gazzetta*, 1901, 31, i, 377—393. Compare this vol., i, 81).—When the compound $\text{C}_{24}\text{H}_{19}\text{ON}$, obtained by the condensation of *β* naphthol, benzaldehyde, and ammonia, and melting at 150° (*loc. cit.*), is boiled with moderately concentrated hydrochloric acid, it undergoes hydrolysis, yielding for each mol. of the compound 1 mol. of benzaldehyde and 1 of *aminobenzylidene-β-naphthol hydrochloride*, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHPh}\cdot\text{NH}_2\cdot\text{HCl}$. The latter separates from hydrochloric acid in long, lustrous, white needles which begin to redden at 190°, and are not completely melted at 220°; it dissolves in boiling water with slight decomposition, and

is very soluble in ethyl or methyl alcohol or acetic acid. In cold aqueous potassium hydroxide it dissolves, imparting a violet fluorescence to the liquid; this solution, when heated, evolves ammonia, whilst when it is kept for a few days, the fluorescence disappears, and is replaced by an orange-yellow colour. The free *aminobenzylidene-β-naphthol*, $C_{17}H_{15}ON$, separates from ether in tufts of long, white needles which melt and decompose at 125° . When boiled with water, in which it is insoluble, or with alcohol or potassium hydroxide solution, which dissolves it, the base decomposes with evolution of ammonia, and, in the case of the last-named solution, of a small quantity of benzaldehyde; it is readily soluble in benzene, acetone, or chloroform, and also in ethyl acetate or acetic acid, undergoing change. With chloroform and potassium hydroxide, it does not give the carbylamine reaction, nor does it yield a colouring matter with furfuraldehyde and acetic acid, as is the case with derivatives containing an amino-group united to the aromatic nucleus. Its *diacetyl* derivative, $C_{21}H_{19}O_3N$, crystallises from dilute alcohol in short, stout prisms melting at 162° . When the base is dissolved in ethyl acetate, intense cooling takes place, and suddenly the liquid is transformed into a voluminous, crystalline paste, which dissolves on further heating with ethyl acetate, the products formed being found to be β -naphthol and the original compound melting at 150° . The latter is also obtained by the condensation of benzaldehyde and aminobenzylidene- β -naphthol in alcoholic solution. From these transformations of the condensation product of β -naphthol, benzaldehyde, and ammonia, the author concludes it must have the constitution



and the name 1:3-*diphenyl-4:2-β-naphthoisoaxazine*. Similarly, the compound $C_{20}H_{23}ON$, obtained from β -naphthol, benzaldehyde, and aniline (*loc. cit.*), is 1:2:3-*triphenyl-4:2-β-naphthoisoaxazine*. It is also obtained by the condensation of benzylideneanil- β -naphthol (see Betti, this vol., i, 81) with benzaldehyde. T. H. P.

Interaction of Nitrobenzene and Aniline in presence of Alkalis. By ALFRED WOHL and W. AUE (*Ber.*, 1901, **34**, 2442—2450).—When equal weights of aniline and nitrobenzene are heated with four times the quantity of coarsely powdered sodium hydroxide, initially at 140° for 2 hours, finally for a short time at 160° , there is formed 30 per cent. of phenazine, along with about 60 per cent. of the theoretical quantity of azobenzene. When perfectly dry sodium hydroxide is used, and the temperature not allowed to rise above 125° , instead of the phenazine there is formed *phenazine-5:10-oxide*,



yellowish-red needles, melts at 226.5° (corr.), and sublimes in a vacuum at $240\text{--}250^{\circ}$; it is a weak base, which is not changed when boiled with acetic anhydride for a short time, although decomposed to form phenazine after boiling for an hour. Reduction with sodium amalgam in

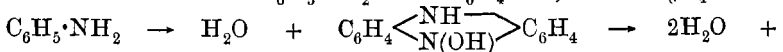
alcohol or with zinc dust and hydrochloric acid yields dihydrophenazine ; the quantitative reduction of the oxide by stannous chloride requires two more hydrogen atoms than the similar reduction of phenazine.

aβ-Naphthaphenazine-7:12-oxide, $C_{10}H_6 \begin{smallmatrix} \diagup N \\ \diagdown O \\ \diagup N \end{smallmatrix} C_6H_4$, obtained along

with *aβ-naphthaphenazine* by the action of dry powdered sodium hydroxide on *β-naphthylamine* and nitrobenzene at 115–140°, forms green crystals which, when powdered and dried, are yellow ; it melts at 182° (corr.), and is easily soluble in all organic solvents. It is shown to contain one oxygen atom more than naphthaphenazine by its quantitative reduction with stannous chloride.

Tolunaphthazine [*methyl-α-β-naphthazine*], $C_{10}H_6 \begin{smallmatrix} \diagup N \\ \diagdown N \end{smallmatrix} C_6H_3Me$, prepared by heating *β-naphthylamine* with *m*-nitrotoluene and dry sodium hydroxide, crystallises from toluene or benzene in yellow needles, melts at 208.5° (corr.), and sublimes under 13 mm. pressure at about 240°.

The formation of phenazine from nitrobenzene and aniline in presence of alkali cannot be due to the intermediate production of azo- or azoxy-compounds, since azobenzene and azoxybenzene fail to yield it in presence of alkali, either alone or with aniline or nitrobenzene. *o*-Nitrophenol, moreover, which is formed by the action of alkali hydroxides on nitrobenzene (Abstr., 1900, i, 157), fails to yield phenazine when fused with aniline and an excess of alkali. It is probable that phenazine is formed thus: I. $C_6H_5 \cdot NO_2 \rightarrow NO \cdot C_6H_4 \cdot OH$; II. $NO \cdot C_6H_4 \cdot OH +$



$C_6H_4 \begin{smallmatrix} \diagup N \\ \diagdown N \end{smallmatrix} C_6H_4$. Nitrobenzene is initially converted into the hypothetical *o*-nitrosophenol (from which *o*-nitrophenol would result by a simple oxidation), and this condenses in the manner shown ; the compound $C_6H_4 \begin{smallmatrix} \diagup NH \\ \diagdown N(OH) \end{smallmatrix} C_6H_4$ cannot be isolated, but probably is the origin of the phenazine-5:10-oxide which is formed from it by the oxidation of two hydrogen atoms.

W. A. D.

Action of Hydrogen Peroxide on Tertiary Bases. III. By MARTIN AUERBACH and RICHARD WOLFFENSTEIN (*Ber.*, 1901, 34, 2411–2415. Compare Abstr., 1899, i, 935).—Nicotine oxide (oxynicotine), obtained by Pinner and Wolffenstein (Abstr., 1891, 473, and 1892, 1010) by the action of hydrogen peroxide on nicotine, is shown to be the oxide of a tertiary base, and to have the constitution $C_5NH_4 \cdot \begin{smallmatrix} CH-CH_2 \\ | \\ O:NMe \cdot CH_2 \end{smallmatrix} > CH_2$. The picrate was found to melt at 155–156°.

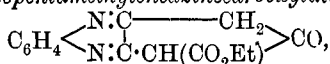
Sulphurous and nitrous acid reduce the oxide to nicotine.

Hydrogen peroxide acts very slowly on *α*- and *β*-dimethylnaphthylamine. Although small quantities of substance containing oxygen were obtained, oxides of the tertiary bases were not found.

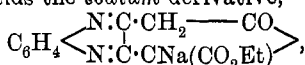
K. J. P. O.

Condensation of Ethyl Cetipate with *o*-Diamines. II. By RENÉ THOMAS-MAMERT and A. STRIEBEL (*Bull. Soc. Chim.*, 1901, [iii], 25, 712—725. Compare Abstr., 1900, i, 459).—*Ethyl quinoxaline-*

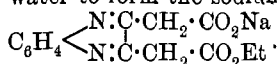
2 : 3-diacetate, $C_6H_4 \begin{smallmatrix} \text{N}:\text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \\ \text{N}:\text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \end{smallmatrix}$, obtained by heating a mixture of ethyl cetipate and *o*-phenylenediamine in alcoholic solution for 1—2 hours at 100°, crystallises from light petroleum in yellow prisms, and melts at 58·2°; with cold dilute aqueous potassium hydroxide (2 mols.), it yields, after several days, a solution which, on adding dilute sulphuric acid, gives a yellow precipitate of indefinite composition. This dissolves in warm sodium carbonate, and the solution on cooling yields the sodium salt, $C_6H_4 \begin{smallmatrix} \text{N}:\text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na} \\ \text{N}:\text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \end{smallmatrix}$, in golden-yellow needles; on adding dilute sulphuric acid to the solution of the sodium salt, *ethyl benzo-β-ketopentamethyleneazinecarboxylate*,



separates in golden-yellow needles, and can be crystallised from chloroform; it decomposes without melting. Ethyl quinoxalinediacetate is not acted on by sodium ethoxide in absolute ethereal solution, but in alcoholic solution yields the sodium derivative,



which crystallises in spherular aggregates of greenish-yellow needles, and is decomposed by water to form the sodium salt,

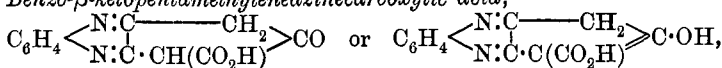


The latter is also readily formed on warming ethyl benzo-β-ketopentamethyleneazinecarboxylate with aqueous sodium carbonate. Ethyl benzo-β-ketopentamethyleneazinecarboxylate, since it fails to yield either an oxime or a hydrazone, and does not lose carbon dioxide and alcohol to form the compound $C_6H_4 \begin{smallmatrix} \text{N}:\text{C}\cdot\text{CH}_2 \\ \text{N}:\text{C}\cdot\text{CH}_2 \end{smallmatrix} \rangle \text{CO}$ when heated

with dilute sulphuric acid, probably exists in the isodynamic form, $C_6H_4 \begin{smallmatrix} \text{N}:\text{C} \text{---} \text{CH}_2 \\ \text{N}:\text{C}\cdot\text{C}(\text{CO}_2\text{Et}) \end{smallmatrix} \rangle \text{C}\cdot\text{OH}$; it does not interact with benzaldehyde save in presence of a trace of piperidine (compare Schiff, Abstr., 1898, i, 237 and 355), when it readily yields the *benzylidene* derivative, $C_6H_4 \begin{smallmatrix} \text{N}:\text{C} \text{---} \text{C}(\text{CHPh}) \\ \text{N}:\text{C}\cdot\text{CH}(\text{CO}_2\text{Et}) \end{smallmatrix} \rangle \text{CO}$, of the ketonic form, which crystallises

from carbon tetrachloride in yellowish-orange leaflets, and melts at 203°. It should be noted, however, that it does not yield an acetyl derivative with acetic anhydride.

Benzo-β-ketopentamethyleneazinecarboxylic acid,



is obtained by hydrolysing the ethyl ester with alcoholic sodium ethoxide (2 mols.), and decomposing the sodium salt, $C_6H_4 \begin{smallmatrix} \text{N}:\text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na} \\ \text{N}:\text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na} \end{smallmatrix}$,

which could not be isolated, with dilute sulphuric acid; it crystallises from alcohol in silky, golden-yellow needles, decomposes without melting at about 200° , and does not lose carbon dioxide to form the compound $C_6H_4 \begin{smallmatrix} N:C \cdot CH_2 \\ N:C \cdot CH_2 \end{smallmatrix} > CO$, when heated for several hours with dilute sulphuric acid. With benzaldehyde in boiling carbon tetrachloride solution in presence of a trace of piperidine, it readily yields the *benzylidene* derivative, $C_6H_4 \begin{smallmatrix} N:C-C(CHPh) \\ N:C \cdot CH(CO_2H) \end{smallmatrix} > CO$, which crystallises in yellow needles and melts at 198° .

Ethyl 6-methylquinoxaline-2:3-diacetate, $C_6H_3Me \begin{smallmatrix} N:C \cdot CH_2 \cdot CO_2Et \\ N:C \cdot CH_2 \cdot CO_2Et \end{smallmatrix}$, obtained from ethyl cetipate and 3:4-tolylenediamine, forms yellow prisms and melts at 59° .

Ethyl methylbenzo-3-ketopentamethyleneazinecarboxylate decomposes without melting at 200° ; its *benzylidene* derivative forms orange-coloured needles and melts at 198° .

Methylbenzo-β-ketopentamethyleneazinecarboxylic acid crystallises in yellow needles and decomposes at about 220° ; its *benzylidene* derivative melts above 200° .

With 1:2:3:4-tetraminobenzene, ethyl cetipate condenses to form *ethyl 1:2:3:4-di-quinoxalinetetracetate* [1:4:7:10-naphthate-tetrazine-2:3:8:9-tetracetate], $C_6H_2 \left(\begin{smallmatrix} N:C \cdot CH_2 \cdot CO_2Et \\ N:C \cdot CH_2 \cdot CO_2Et \end{smallmatrix} \right)_2$, which crystallises from alcohol in brownish-yellow, silky needles and melts at 128° ; the analogous compound from 1:2:4:5-tetraminobenzene forms orange leaflets and melts at 143° , that from 2:3:4:5-tetraminotoluene forming silky, yellow needles and melting at 153° . Alcoholic sodium ethoxide converts the last of these into the compound $C_{23}H_{20}O_6N_4$, which is a yellow powder decomposing at 220° . W. A. D.

Isatin and its Derivatives. By LEO MARCHLEWSKI and J. SOSNOWSKI (*Ber.*, 1901, **34**, 2294—2298).—By the action of nitrous acid, isatic acid is converted into *o*-hydroxybenzoylformic acid, $OH \cdot C_6H_4 \cdot CO \cdot CO_2H$, which forms a yellow *sodium* salt, and condenses with *o*-phenylenediamine to 2-hydroxy-3-*o*-hydroxyphenylquinoxaline, $OH \cdot C_6H_4 \cdot C \begin{smallmatrix} N-C_6H_4 \\ C(OH):N \end{smallmatrix}$, thus confirming the constitution assigned to the latter compound (this vol., i, 415). By distilling the barium salt of the sulphonic acid, the dihydroxy-compound is converted into coumarophenazine, $\begin{smallmatrix} C_6H_4 \cdot C:N \\ O-C:N \end{smallmatrix} > C_6H_4$.

Ethoxycoumarophenazine, $\begin{smallmatrix} C_6H_4 \cdot C:N \cdot C \cdot CH \cdot C \cdot OEt \\ O-C:N \cdot C \cdot CH \cdot CH \end{smallmatrix}$, prepared by the action of nitrous acid on the condensation product of acetylisatin with ethoxy-*o*-phenylenediamine, crystallises in minute, white needles and melts at 162.5° .

*2-Hydroxy-7-ethoxy-3-*o*-hydroxyphenylquinoxaline*,



prepared by the action of ethoxy-*o*-phenylenediamine on hydroxybenzoyl-formic acid, crystallises in yellow needles and melts at 242—243°.

T. M. L.

Constitution of Urazines. By MAX BUSCH (*Ber.*, 1901, **34**, 2311—2320. See this vol., i, 488).—The following new compounds, obtained by methods previously described (*loc. cit.*), were prepared:—*ethyl 2-phenyl-5-methylphenylcarbazide-1-carboxylate*, which crystallises in small, colourless needles and melts at 164—165°; *ethyl 2-phenyl-4-methylphenylsemicarbazidecarboxylate*, which crystallises in prisms melting at 117°; *1-phenyl-4-methylanilinourazole*, $\begin{matrix} \text{N}:\text{C}(\text{OH}) \\ | \\ \text{NPh}\cdot\text{CO} \end{matrix} > \text{N}\cdot\text{NMePh}$,

which crystallises in lustrous, colourless leaflets, melts at 167—168°, forms a *methyl* ether which crystallises in clusters of small needles softening at 101° and melting at 103°, and, when treated with hydriodic acid, forms 1-phenyl-4-anilinourazole; *ethyl 2-phenyl-4:5-dibenzylcarbazide-1-carboxylate*, which crystallises in four-sided tablets, melts at 105°, and, when treated with alcoholic potash, yields *phenyldibenzylurazine*, $\begin{matrix} \text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{CO}\cdot\text{NPh} \\ | \\ \text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{CO}\cdot\text{NH} \end{matrix}$, which crystallises in colourless leaflets, melts at 180°, has a neutral reaction, and is the first known urazine (see Busch, *loc. cit.*).
R. H. P.

Syntheses in the Urazole Series. By MAX BUSCH and ALFRED GROHMANN (*Ber.*, 1901, **34**, 2320—2331).—Urazoles and thiourazoles (from the thiocarbazides $\text{NR}'_2\cdot\text{NH}\cdot\text{CS}\cdot\text{NR}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$) have been prepared by methods previously described (this vol., i, 488). *Ethyl 2-phenyl-5-p-anisylcarbazide-1-carboxylate* crystallises in small, colourless needles and melts at 161—162°. *Ethyl 2-p-anisyl-5-phenylcarbazide-1-carboxylate* crystallises in aggregates of small, slender needles and melts at 184°. *Ethyl α -naphthylcarbazinate* crystallises in leaflets and melts at 107—108°, and the *chloride*, $\text{C}_{10}\text{H}_7\cdot\text{N}(\text{COCl})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, melts about 115°; *1- α -naphthyl-4-aminourazole* crystallises in compact tablets, which soften at 196° and melt at 201°. *Ethyl β -naphthylcarbazinate* crystallises in needles and melts at 105.5°; the analogous chloride crystallises in silky needles and melts at 139°, and *1- β -naphthyl-4-aminourazole* crystallises in lustrous, white leaflets melting at 265°. The naphthylaminourazoles, when treated with nitrous acid, yield the naphthylurazoles, *α -naphthylurazole* crystallises in clusters of lustrous, small needles melting at 233—234°, and *β -naphthylurazole* in mossy needles melting at 287°.

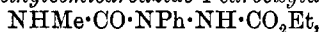
Ethyl 2:4-diphenylthiosemicarbazide-1-carboxylate, $\text{NPh}\cdot\text{CS}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, crystallises in slender needles, melts at 145°, and, when hydrolysed, yields *1:4-diphenyl-5-thiourazole*, $\begin{matrix} \text{N}:\text{C}(\text{OH}) \\ | \\ \text{NPh}-\text{CS} \end{matrix} > \text{NPh}$, which crystallises in small, slender needles melting at 214—215°. *4-Amino-5-thio-1-phenylurazole* crystallises in felted needles, melts and decomposes at 191—192°, and, when treated with nitrous acid, yields *5-thio-1-phenylurazole*, which crystallises in laminae melting at 229—230°, and a microcrystalline powder melting at 220°, which is probably a *disulphide*. *Ethyl 2:5-phenylthiocarbazide-1-carboxylate* crystallises in white

leaflets melting at 138° , and 5-thio-1-phenyl-4-anilinourazole melts at 184° . Ethyl-2-phenyl-5-p-tolylthiocarbazide-1-carboxylate crystallises in clusters of small needles melting at 133° , and 5-thio-4-p-toluidino-1-phenylurazole in slender needles melting at 190° . Ethyl p-tolylhydrazine- α -thiocarbonylchloride- β -carboxylate was obtained in the form of yellowish needles melting at 109 – 110° , ethyl 5-phenyl-2-p-tolylthiocarbazide-1-carboxylate as compact crystals melting at 125° , and 5-thio-4-anilino-1-p-tolylurazole as slender needles melting at 219° .

R. H. P.

1:4-Dialkylurazoles. By MAX BUSCH and C. HEINRICHS (*Ber.*, 1901, 34, 2331–2339).—The α -carbonyl chlorides of carbazates react with primary amines, forming 2:4-dialkylsemicarbazide-1-carboxylates, which, when hydrolysed, yield 1:4-dialkylurazoles.

Ethyl 2-phenyl-4-methylsemicarbazide-1-carboxylate,



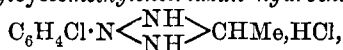
crystallises in colourless needles and melts at 131° ; 1-phenyl-4-methylurazole, $\text{NPh}-\text{N} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C}(\text{OH}) \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{CO}\cdot\text{NMe}$, crystallises in lustrous, colourless needles,

melts at 224° , forms a sodium salt which crystallises in lustrous, small, felted needles, and, when treated with acetic anhydride and sodium acetate, an acetyl derivative which crystallises in colourless needles and melts at 129° . Ethyl 2-phenyl-4-methylsemicarbazide-1-carboxylate crystallises in nodules of small, colourless needles melting at 113° ; 1-phenyl-4-methylurazole crystallises in lustrous laminæ and melts at 174° . Ethyl 2-phenyl-4-benzylsemicarbazide-1-carboxylate crystallises in clusters of needles melting at 143 – 144° , and 1-phenyl-4-benzylurazole in tablets melting at 232° . Ethyl 2:4-diphenylsemicarbazide-1-carboxylate crystallises (with $\frac{1}{2}\text{EtOH}$) in prisms melting at 123° (without the alcohol of crystallisation at 131°); 2:4-diphenylurazole crystallises in lustrous leaflets, melts at 163° , and forms potassium (small, felted needles), sodium (lustrous needles), and calcium salts (microscopic leaflets), an acetyl derivative, which crystallises in long, silky needles melting at 166° , and a methyl ether (probably), $\text{NPh}-\text{N} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C}(\text{OMe}) \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{CO}\cdot\text{NPh}$,

which crystallises in long, brittle needles melting at 134° . Ethyl 2-phenyl-4-p-tolylsemicarbazide-1-carboxylate crystallises in leaflets melting at 134° , and 1-phenyl-4-p-tolylurazole in small, slender, felted needles melting at 189 – 190° . Ethyl p-tolylcarbazinate crystallises in pale yellow, compact needles melting at 89 – 90° , the chloride of the α -carboxylate in small, white needles melting at 94° , ethyl 4-phenyl-2-p-tolylsemicarbazide-1-carboxylate in very lustrous, flat needles melting at 96 – 97° , and 4-phenyl-1-p-tolylurazole in lustrous laminæ which soften at 195° and melt at 201° .

R. H. P.

Triazan Derivatives. III. By HUGO VOSWINCKEL (*Ber.*, 1901, 34, 2349–2354. Compare *Abstr.*, 1899, i, 958, and this vol., i, 53).—p-Chlorophenylmethylcyclomethylenetriazan hydrochloride,



is prepared by reducing chlorophenylmethoxycyclomethylenetriazan with stannous chloride in alcoholic solution (*loc. cit.*); from hydro-

chloric acid, the salt crystallises in colourless leaflets, from alcohol and ether in prisms containing alcohol which melt at 100° ; the dry salt melts at 197° . The free base is an oil which readily decomposes.

On reducing chlorophenylmethoxycyclomethylenetriazan with a boiling aqueous solution of ammonium sulphide, *p*-chlorophenylhydrazine (m. p. 88°) is formed.

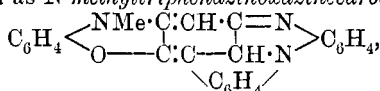
All attempts to prepare derivatives of phenyltriazan by reduction of phenylnitrosohydrazine or its acyl derivatives failed.

Benzoylphenylnitrosohydrazine, $\text{NO}\cdot\text{NPh}\cdot\text{NHBz}$, prepared by the action of nitrous acid on benzoylphenylhydrazine in alcoholic suspension, crystallises in yellow needles melting and decomposing at 110° . This substance gives Liebermann's reaction, dissolves in sulphuric acid forming a carmine solution, and also in aqueous alkalis and ammonia.

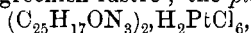
Potassium phenylnitrosohydrazine sulphonate, $\text{NO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{SO}_3\text{K}$, prepared by the action of nitrous acid on potassium phenylhydrazine-sulphonate, forms yellowish-white needles which decompose at 250° , dissolve readily in alkalis, and give Liebermann's reaction.

K. J. P. O.

Base from N-Methyltriphenoxazinephenazonium Salts (N-Methyltriphenazinoxazinecarbazole). By EMIL DIEPOLDER (*Ber.*, 1901, 34, 2272—2276).—*N-Methyltriphenoxazinephenazonium nitrate*, $\text{C}_{25}\text{H}_{18}\text{O}_4\text{N}_4\cdot 2\text{H}_2\text{O}$, crystallises in golden needles; it is prepared in manner similar to the chloride (*Abstr.*, 1900, i, 192), but a better yield is obtained. The chloride is reduced to a leuco-compound by stannous chloride, or by zinc dust and acetic acid. Sodium hydroxide precipitates from a solution of the nitrate an *anhydro-base*, $\text{C}_{25}\text{H}_{17}\text{ON}_3$, which is regarded as *N-methyltriphenazinoxazinecarbazole*,



the hydroxyl group being assumed to wander from the nitrogen atom to a carbon atom, and then to be eliminated with a hydrogen atom to form a new five-membered ring; the base contains seven rings and is exceedingly stable; it does not melt at 330° , is not attacked by sodium acetate and acetic anhydride, and is not decomposed by heating at 200° with dilute sulphuric acid; it is obtained in needles with a bronze-like lustre when sublimed, or when crystallised from ethyl benzoate, but crystallises from nitrobenzene or benzene with a green lustre; it dissolves in 25 parts of boiling nitrobenzene, 30 parts of boiling ethyl benzoate, 200 parts of boiling chloroform, and 600 parts of boiling benzene. The *hydrochloride*, $\text{C}_{25}\text{H}_{17}\text{ON}_3\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$, forms needles having a greenish lustre; the *platinichloride*,



is a flocculent, blue precipitate. When decomposed by alkalis, the *anhydro-base* gives methyl-*o*-aminophenol, hydroxyyaposafrazone, and a substance which melts at 240° , crystallises from a mixture of benzene and alcohol in brown needles with a green lustre, and is perhaps

o hydroxymethylanilinoaposafrane, $\text{N} = \text{C}_6\text{H}_2 - \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$
 $\text{C}_6\text{H}_4 \cdot \text{NPh} > \text{O}$

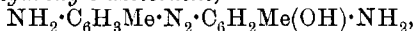
T. M. L.

Azo-derivatives of *o*-Nitro-*p*-toluidine. By KARL ELBS and B. SCHWARZ (*J. pr. Chem.*, 1901, [ii], 562—568).—The mixture of *p*-diamino-*o*-azoxytoluene and *p*-diamino-*o*-azotoluene, obtained in the electrolytic reduction of *o*-nitro-*p*-toluidine (*Abstr.*, 1899, i, 270), forms mixed crystals melting at 132—133°; the two substances can only be separated by recrystallisation of their hydrochlorides. The pure azo-derivative can be obtained free from the azoxy-compound by converting the latter into diaminohydroxyazotoluene by means of sulphuric acid.

p-Diamino-*o*-azoxytoluene, $N_2O(C_6H_3Me \cdot NH_2)_2$, crystallises in golden-yellow, silky needles melting at 148—148.5°; the *dihydrochloride* forms pale yellow, lustrous leaflets, which decompose on heating without melting; the *platinichloride*, pale yellow, microscopic needles; the *sulphate*, yellowish needles. The *diacetyl* derivative, $C_{14}H_{14}ON_4(OAc)_2$, forms dirty yellow crystals, melting and decomposing at 280—281°.

p-Diamino-*o*-azotoluene, $N_2(C_6H_3Me \cdot NH_2)_2$, prepared most easily by the oxidation of the corresponding hydrazo-derivative by sodium hydroxide and air, forms dark red needles, or bronze-coloured leaflets melting at 158—159°. The *hydrochloride* crystallises in thin, pale brown leaflets, which decompose without melting, and are less soluble in dilute hydrochloric acid than the hydrochloride of the azoxy-derivative; the *platinichloride* forms a pale brown powder; the *sulphate*, microscopic, pale brown needles.

p-Diamino-*m*-hydroxy-*o*-azotoluene,



is prepared by the action of concentrated sulphuric acid at 100° on *p*-diamino-*o*-azoxytoluene; on pouring the product into water, the sulphate separates. The hydroxyazo-compound crystallises in deep red needles melting and decomposing at 176—178°; the *sulphate* forms dark reddish-brown leaves.

p-Diamino-*o*-hydrazotoluene, $N_2H_4(NH_2 \cdot C_6H_3Me)_2$, is best prepared by the electrolytic reduction either of the azo- or the azoxy-compound, or of a mixture of the two dissolved in dilute alcohol, in the presence of sodium acetate; the yield is 80 per cent. of the calculated quantity (compare *loc. cit.*).
K. J. P. O.

Sensitiveness of Diazo-compounds, especially of 3-Diazo-carbazole, to Light. Some new Derivatives of Carbazole. By OTTO RUFF and VICTOR STEIN (*Ber.*, 1901, 34, 1668—1684).—The following methods give beautiful, brown photographic prints, with clear, permanent tones; the first method is used for positives and the second for negatives.

I. A gelatin photographic paper, hardened with formaldehyde, is saturated on the prepared side with a 2 per cent. solution of diazo-carbazole zincchloride, dried, and exposed to light passing through the positive; the print is developed and fixed by a 1 per cent. alkaline solution of α -naphthol, which produces an orange-yellow picture which is toned to brown by a bath of dilute acetic acid. The light passing through the clear parts of the positive destroys the diazo-salt and renders it unable to combine with the naphthol to form a dye. Using

β -naphthol, phloroglucinol, resorcinol, or *m*-tolylenediamine instead of α -naphthol, dark red, violet, yellowish-brown, or brownish-violet prints are respectively obtained.

II. The paper is soaked in a solution containing sodium carbazole-diazosulphonate and a naphthol or an amine, dried, and exposed under the negative; where light passes through, the formation of a dye occurs, and the print is fixed by washing with hot water, dilute sodium hydroxide, cold water, dilute acetic acid, and finally water. The following colours are produced by certain naphthols; α -naphthol brown, β -naphthol red, 2-naphthol-6- and -4-sulphonic acids violet, the 3:6-disulphonic acid bluish-violet, and *m*-tolylenediamine brown.

The prints are permanent, and the original unexposed paper can be kept for long periods without ill effects.

The following facts are established with regard to the action of light on substituted diazobenzene chlorides. Those which contain a negative group (OH , NO_2 , CO_2H) in the para-position are more sensitive than those containing a similarly situated positive group (Cl , CH_3); the influence of the nitro-group is greatest. Ortho- and para-substituted groups have about the same effect, either in increasing or decreasing sensitiveness; this effect is always less than the effect of a meta-group. In the case of diazo-salts derived from different nuclei, the sensitiveness to light increases with the "number of atoms in the nucleus"; thus the diazo-salt from 3-aminocarbazole is nearly five times as sensitive as that from *p*-toluidine. As regards the decomposition of diazo- and tetrazo-compounds, an equal number of diazo-groups are destroyed by light in the same time; thus the same number of minutes is necessary to decompose completely the diazo-salt from an *N*/40 solution of *p*-aminodiphenyl as from an *N*/20 solution of benzidine.

Nitroso-3-nitrocarbazole, obtained by passing gaseous nitrous acid, evolved from starch and nitric acid, into carbazole dissolved in glacial acetic acid, crystallises from alcohol in bright yellow needles, melts at 166.5° (corr.), and on boiling with amyl alcohol yields 3-nitrocarbazole (m. p. 208.5° corr.; Mazzara, *Abstr.*, 1891, 570, and Votočka, *Rozpravy české Akad.*, 5, ii, No. 22, give 209° and 210° respectively). When reduced with stannous chloride, it gives 3-aminocarbazole, which darkens at 240° and melts and decomposes at 259° (corr., Mazzara gives $246\text{--}248^\circ$, Votočka 248° and 256°). 3-Diazocarbazole chloride yields well-defined salts with zinc chloride and mercuric chloride; the dyes derived from it are of small tinctorial value. *Sodium carbazole-diazosulphonate* apparently exists in two modifications; the *labile* form is orange-yellow and changes to the *stable* form on heating with water, from which the latter crystallises in needles. When reduced with sodium amalgam, *sodium carbazole-3-hydrazinosulphonate* is obtained in yellowish, ill-defined crystals. 3-Hydroxycarbazole is only formed in small quantity (10 per cent.) on boiling 3-diazocarbazole with water; it crystallises from xylene in small, feebly yellow needles, melts at $260\text{--}261^\circ$ (corr.), and yields a *diacetyl* derivative, crystallising in colourless needles and melting at $113\text{--}114^\circ$.

When 3-aminocarbazole is heated with acetic anhydride for 8 hours at 180° , a mixture of the *diacetyl* and *triacetyl* derivatives is obtained;

the former crystallises from absolute alcohol in microscopic needles and melts at 199.5° (corr.), whilst the latter forms larger needles and melts at 174.5° (corr.). On nitration at 60° , the triacetyl derivative yields *nitrodiacetyl-3-aminocarbazole*, which crystallises from alcohol in small, yellow needles and melts at 199.5° (corr.).

W. A. D.

Action of Alkylmalonic Esters on Diazonium Chlorides. By G. FAVREL (*Compt. rend.*, 1901, 132, 1336—1338).—The alkylmalonic esters react with diazonium chlorides in accordance with the following equation, $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OH} + \text{CHR}(\text{CO}_2\text{Et})_2 = \text{Ph}\cdot\text{NH}\cdot\text{N}:\text{CR}\cdot\text{CO}_2\text{Et} + \text{CO}_2 + \text{Et}\cdot\text{OH}$, yielding substituted hydrazones of the pyruvic acid series. The reaction has been generalised by employing the ethyl esters of both methyl- and ethyl-malonic acids and the diazonium salts derived from aniline and the toluidines.

G. T. M.

Synthesis of *o*-Azidobenzaldehyde [*o*-Triazobenzaldehyde]. By EUGEN BAMBERGER and ED. DEMUTH (*Ber.*, 1901, 34, 2292—2293).—*o*-Triazobenzaldehyde, $\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{N}_3$, can be synthesised by the action of azoimide on *o*-diazobenzaldehyde, and is identical with the substance prepared indirectly from indiazonoxime (this vol., i, 392).

T. M. L.

Combination of Sodium Tetrazoditolylidisulphonate with β -Naphthylethylamine. Production of a Colouring Matter. By ALPHONSE SEYEWETZ and BLANC (*Compt. rend.*, 1901, 133, 38—41).—The action of β -naphthylethylamine hydrochloride on sodium tetrazoditolylidisulphonate in presence of water yields a yellow oil which gradually becomes crystalline, and can be recrystallised from dilute alcohol (3:10) at a temperature not exceeding 80° . It has the composition $\text{C}_{12}\text{H}_6\text{Me}_2[\text{NH}\cdot\text{N}(\text{SO}_3\text{H})\cdot\text{C}_{10}\text{H}_6\cdot\text{NHEt}]_2$, decomposes at about 160° without melting, and is insoluble in ether, benzene, or chloroform. When exposed to light, it is converted into a red colouring matter. $\text{C}_{12}\text{H}_6\text{Me}_2(\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NHEt})_2$, which decomposes at 150° without melting, is somewhat soluble in alcohol, very slightly so in ether, and insoluble in dilute acids, but dissolves readily in acetone or acetic acid. It is identical with the colouring matter obtained by the action of naphthylethylamine hydrochloride on tetrazotolidine.

C. H. B.

Precipitability of Proteids by Chloroform. By FRIEDRICH KRUGER (*Zeit. Biol.*, 1901, 41, 341—359).—The paper is largely occupied with a discussion of the results of others relating to the applicability of chloroform as a means of precipitating and separating proteids. Special attention was given to a proteid named *mucosalbumin*, which was precipitated by chloroform from extracts of mucous membranes of the stomach and intestine. Analyses do not give concordant results.

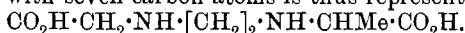
W. D. H.

Compounds of certain Proteids with Hydrogen Chloride. By WALTER ERB (*Zeit. Biol.*, 1901, 41, 309—330).—Proteids behave toward hydrogen chloride as bases, and form salts with it. These proteid salts show hydrolytic dissociation to a great extent, and thus

the various contradictory statements regarding the acid compounds of proteids are explained.

Hetero-albumose, phyto-vitellin, egg-albumin, and serum-albumin were the proteids experimented with, and were prepared in a pure condition. They show different maximal acid capacities, and dissociation curves of different slopes. These properties are regarded as characteristic of the individual proteids. W. D. H.

Glucoproteins as new chemically definite Culture Media for the Study of Micro-organisms. By CHARLES LEPIERRE (*Compt. rend.*, 1901, 133, 113—116).—In the glucoproteins, the author finds a simple material of definite chemical character, from which a great number of micro-organisms (pathogenic and otherwise) are able to obtain their nitrogen. By the hydrolysis of proteids or gelatin at 100° by barium hydroxide (a modification of Schützenberger's method, *Abstr.*, 1886, 270), a series of glucoproteins have been prepared in a pure and crystalline state. They have the general formula $C_nH_{2n}O_4N_2$ (where $n = 6-11$); from gelatin, the members of the series with six and seven carbon atoms have been obtained; from albumin or fibrin, the members with 8, 9, 10, and 11 carbon atoms. The constitution of the substance with seven carbon atoms is thus represented:



The culture-media consist of water (100 grams), glucoprotein (1.5—2 grams), glycerol, dextrose, or sucrose (2—3 grams), sodium chloride and magnesium sulphate (each 0.5 gram), calcium glycerophosphate (0.2—0.3 gram), and potassium hydrogen carbonate (0.1—0.2 gram).

The author has observed that certain bacteria prefer certain glucoproteins. K. J. P. O.

Action of Nascent Chlorine on Casein. By JOSEF HABERMANN and R. EHRENFELD (*Zeit. physiol. Chem.*, 1901, 32, 467—475).—Casein is dissolved in 5 per cent. potassium hydroxide mixed with finely divided potassium chlorate, and treated for some 48 hours at the ordinary temperature with hydrogen chloride. A flocculent precipitate is produced on the addition of water, and this, although free from phosphorus and containing some 13—14 per cent. of chlorine yields, on treatment with hydrochloric acid and stannous chloride, with bromine water or on fusion with potassium hydroxide, products practically identical with those obtained from casein itself under similar treatment. J. J. S.

Formation of Leucinimide by the Peptic and Trypsic Fermentation of Oxyhæmoglobin and of Globin. By SERGEI SALASKIN (*Zeit. physiol. Chem.*, 1901, 32, 592—597).—A leucinimide melting at 295—296°, and apparently identical with the substance described by Cohn (*Abstr.*, 1896, i, 658), has been obtained by the trypsin fermentation of oxyhæmoglobin. A similar compound is also formed by the peptic fermentation of this substance, but no product of definite melting point was obtained, fusion occurring at temperatures ranging from 250° to 273—274°. J. J. S.

Proteinochrome. By FERD. KLUG (*Pflüger's Archiv*, 1901, 86, 194—198).—Pancreatic tissue was allowed to digest itself, and the product shaken with alcohol and ether and centrifugalised; the substance, *proteinochrome*, which gives the characteristic violet-red coloration with chlorine water is present in the lowest strata. By repeated centrifugalising with ether, it is claimed that the substance was obtained in a pure condition, and to it the formula $C_4H_8O_2N$ is assigned.
W. D. H.

Preparation and Analysis of some Nucleic Acids. By P. A. LEVENE (*Zeit. physiol. Chem.*, 1901, 32, 541—551).—In addition to the analyses previously given (this vol., i, 299), numbers are now given for acids obtained from spleen and from yeast.

| Nucleic acid from | C. | H. | N. | P. |
|-------------------|-------|------|-------|------|
| Spleen | 36.40 | 5.24 | 17.30 | 9.03 |
| Yeast | 36.65 | 4.57 | 17.89 | 8.93 |

J. J. S.

Albumin Peptones. By CARL PAAL (*Chem. Centr.*, 1901, i, 1338—1339; from *Festschr. Univ. Erlangen zur Feier S. K. H. des Prinz-regenten Luitpold*. Compare Abstr., 1898, i, 456).—Albumin peptones have been isolated from the mixture of hydrochlorides of albumoses and peptones obtained by digesting egg-albumin with dilute hydrochloric acid. In one case, the albumoses were removed by saturating the aqueous solution with ammonium sulphate. The concentrated solution of the free peptones prepared from the hydrochlorides, when poured into absolute alcohol, gave a precipitate which contained C 44.50 and N 14.87, whilst the filtrate yielded a residue containing C 47.77 and N 12.55 per cent. In a second experiment, the albumoses were removed by saturating the aqueous solution with zinc sulphate, and treating the filtrate with phosphotungstic acid. The solution of the peptones obtained from the precipitate in this case gave a precipitate with alcohol which contained C 50.10 and N 15.58, the residue from the filtrate containing C 52.63 and N 13.76 per cent. The filtrate from the phosphotungstic acid precipitate after removing the acids yielded a peptone insoluble in alcohol and containing C 40.71 and N 9.6, and a soluble peptone containing C 44.28 and N 11.37 per cent. Both these substances give only a faint biuret reaction, and are to be regarded as intermediate products, being related, on the one hand, to the real peptones which are precipitated by phosphotungstic acid, and on the other hand to the amino-acids. The peptones obtained in the first case by means of ammonium sulphate must therefore consist of a mixture of real peptones with intermediate products.
E. W. W.

Intracellular Diastases of the Amœba. By H. MOUTON (*Compt. rend.*, 1901, 133, 244—246).—A species of amœba existing abundantly in garden soil was found to contain a diastase capable of liquefying gelatin and digesting dead microbes in presence of chloroform. It also acts distinctly on albumin coagulated by heat, but

seems to be without action on fibrin previously heated to 58° . The activity of the diastase is shown only in feebly alkaline media and is destroyed at a temperature of 60° .
C. H. B.

Production of Casease by a Parasitic Streptothrix. By E. BODIN and C. LENORMAND (*Ann. Inst. Pasteur*, 1901, 15, 279—288).—The parasitic *Streptothrix*, *Oospora* of the *Microsporum*, found in the horse (*Arch. de parasit.*, 1899, 362 and 606), forms, in culture liquids, a diastase which, like rennet, coagulates casein and casease. The largest amount of casease formed in neutral media, which contain dextrose and peptone, is found when the whole of the dextrose has been assimilated. Casease liquefies gelatin.
R. H. P.

Synthetic Action of the Maltase of Yeast. By OSKAR EMMERLING (*Ber.*, 1901, 34, 2206—2207).—A reply to Hill (this vol., i, 452).
R. H. P.

Contribution to the Study of the Oxydases. By J. SARTHOU (*J. Pharm.*, [vi], 13, 464—465).—Schinoxydase (Abstr., 1900, i, 575), purified by dialysis followed by precipitation by alcohol, contained N, 6.283; S, 0.210; ash (containing iron and calcium), 1.336 per cent. with unweighable traces of phosphorus. This composition suggests that schinoxydase should perhaps be classed with the nucleins. It somewhat resembles an enzyme extracted by Slowtsoff from potato and cabbage, with the difference, however, that the enzyme from potato contains no phosphorus, and acts in a feebly alkaline medium, whilst schinoxydase acts in a neutral one. The author believes that although all the known oxidising enzymes may belong to one group of compounds, they are nevertheless specifically distinct substances, and that for the production of a given phenomenon one of them could not be replaced by another.
M. J. S.

***o*-Mercuridibenzoic Acid.** By LEONE PESCI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 413. Compare Abstr., 1900, i, 546).—*Sodium o-sulphomercuribenzoate*, $S(Hg \cdot C_6H_4 \cdot CO_2Na)_2$, obtained by mixing concentrated solutions of equivalent quantities of sodium *o*-hydroxymercuribenzoate and sodium sulphide, crystallises from alcohol in thin needles. The corresponding acid forms a readily decomposable, gelatinous mass. When an aqueous solution of the sodium salt is boiled in a reflux apparatus, mercuric sulphide separates and sodium *o*-mercuridibenzoate is obtained.

o-Mercuridibenzoic acid, $Hg(C_6H_4 \cdot CO_2H)_2$, crystallises from alcohol in shining needles which are insoluble in water and on heating decompose without melting. Its calcium salt separates from water in white, mammillary masses.
T. H. P.

Organic Chemistry.

Polymerisation of Diisopropenyl. By IWAN L. KONDAKOFF (*J. pr. Chem.*, 1901, [ii], 64, 109—110. Compare this vol., i, 62).—Diisopropenyl is partially polymerised by alcoholic potash (*loc. cit.*). If it is exposed to diffused light for several months, air being excluded, it becomes completely transformed into a white solid, which resembles indiarubber in properties, is insoluble in most solvents, but soluble in benzene, and reacts with bromine, evolving hydrogen bromide. K. J. P. O.

Action of Ethyl Alcohol on Barium Ethoxide. Synthesis of *n*-Butyl Alcohol. By MARCEL GUERBET (*Compt. rend.*, 1901, 133, 300—302. Compare Abstr., 1899, i, 471, 472, and this vol., i, 182, and 307).—*n*-Butyl alcohol is formed when a concentrated (28.5 per cent.) solution of barium ethoxide in ethyl alcohol is heated in sealed tubes at 230—240° for about 3 days, the yield being 3 grams from 500 grams of the ethoxide. J. J. S.

Oxidation of Propylene Glycol by *Mycoderma Aceti*. By ANDRÉ KLING (*Compt. rend.*, 1901, 133, 231—233).—Propylene glycol is oxidised by *Mycoderma aceti* in much the same way as by the sorbose bacterium (Abstr., 1899, i, 323; 1900, i, 129), and is converted into acetol, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$. C. H. B.

Isomeric *iso*Butylene Chlorohydrins and the Decomposition of Mixed Ethers by Hydrogen Haloids. By ARTHUR MICHAEL [and, in part, V. L. LEIGHTON and F. D. WILSON] (*J. pr. Chem.*, 1901, [ii], 64, 102—109. Compare Abstr., 1900, i, 321).—The chlorohydrin obtained by Butleroff (*Annalen*, 1860, 144, 125) from *iso*-butylene and hypochlorous acid and investigated by Henry (*Bull. Soc. Chim.*, 1876, [ii], 26, 24), was thought by them to be represented by the formula $\text{CMe}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$. In the case of propylene and hypochlorous acid, the author found (*loc. cit.*) that the hydroxyl group became attached to the carbon atom poorest in hydrogen. *iso*Butylene chlorohydrin boils at 128—129°, and has a sp. gr. 1.0663 at 20°. Since with phosphoric oxide this chlorohydrin yields the two chloro*iso*-butylenes $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}_2\text{Cl}$ and $\text{CMe}_2\cdot\text{CHCl}$, it has the formula $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Cl}$. Of the two chloro*isobutylenes*, dimethylchloroethylene is not attacked by boiling alcoholic potash, and represents 75 per cent. of the mixture.

*iso*Butylene oxide yields, with hydrogen chloride, a mixture of two chlorohydrins, $\text{CMe}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ and $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Cl}$. The mixture boils at 127—130°, and has a sp. gr. 1.0587 at 20°.

The decomposition of mixed ethers by hydrogen haloids, according to Ferreira da Silva (*Ann. Chim. Phys.*, 1875, [v], 7, 429), results in the halogen becoming attached to the smaller alkyl radicle. The author finds that ethyl propyl ether and hydrogen iodide yield 2 parts of ethyl iodide and 1 part of propyl iodide; propyl *isopropyl* ether both propyl

and *isopropyl iodide*, but methyl propyl ether gives only traces of propyl iodide. From these and earlier experiments (*loc. cit.*), the author deduces rules for the decomposition of mixed ethers by hydrogen haloids.

K. J. P. O.

Action of Sulphuric Acid on the Glycol from *iso*Butaldehyde and *iso*Valeraldehyde. By VICTOR LOWY and FRITZ WINTERSTEIN (*Monatsh.*, 1901, 22, 398—414. Compare Lilienfeld and Taus, Abstr., 1898, i, 508).—When the glycol (Fossek, Abstr., 1891, 31) is heated with 30 per cent. sulphuric acid for 8 hours at 150°, it yields on fractional distillation three liquids boiling respectively at 112°, 140°, and 175° under the ordinary pressure, and a fourth boiling at 140° under 18 mm. pressure. The first of these is a *hydrocarbon*, C_9H_{16} , which does not solidify at -18°, with bromine yields a *dibromide*, and on oxidation with aqueous potassium permanganate gives a mixture of *isobutyric* and *isovaleric* acids; its structure is therefore probably

$$\begin{array}{c} CH_2 \\ | \\ CMe_2 \end{array} > C:CHPr^s.$$

The substance boiling at 140°, $C_9H_{18}O$, does not interact with zinc ethyl and fails to yield an oxime; it is therefore not an aldehyde, but probably an oxide, $\begin{array}{c} CH_2 \cdot CHPr^s \\ | \\ CMe_2 - CH_2 \end{array} > O$ or $\begin{array}{c} CH_2 \cdot O \\ | \\ CMe_2 \end{array} > CH \cdot CH_2Pr^s$. The substance boiling at 140° under 18 mm. pressure is an *oxide*, $C_{18}H_{36}O_2$, which is not changed by digesting with water for 10 hours at 100°; it regenerates the parent glycol on heating with 50 per cent. hydrobromic acid for 6 hours at 150°, and boiling the product for 10 hours with aqueous potassium carbonate.

The liquid boiling at 175° is apparently not a pure substance; analyses point to the formula $C_6H_{12}O$, but its molecular weight is about 150—160. It does not interact with either zinc ethyl or acetic anhydride.

W. A. D.

Dissociation of the Alkyl Nitrates, Sulphates, and Haloids. By JOHN U. NEF (*Annalen*, 1901, 318, 1—57. Compare Abstr., 1900, i, 4).—Olefines and mixed ethers are simultaneously produced when the alkyl haloids are treated with sodium ethoxide or alcoholic potassium hydroxide. The formation of the hydrocarbons was formerly assumed to be due to an "alkylene" decomposition, but since the alkyl nitrates and the mono- and di-alkyl sulphates do not yield olefines under these conditions, the author now supposes that, in all cases, the first change is an "alkylidene dissociation," and that if an unsaturated hydrocarbon is liberated, its production is due to a subsequent rearrangement of the alkylidene.

The above generalisation, however, does not hold in the case of a tertiary nitrate, for bromotrimethylcarbyl nitrate, $NO_2 \cdot O \cdot CMe_2 \cdot CH_2Br$, when treated with alcoholic potassium hydroxide readily yields bromo*iso*-crotyl. A study of the interaction of the butyl chlorides and iodides with sodium butyloxide shows that in every case *isobutylene* and an ether are produced; the decomposition of amyl chloride and iodide by sodium ethoxide gives rise to amylene and the mixed ether, and the slower the rate of decomposition the greater is the yield of ether.

n-Propyl sulphate, conveniently prepared by heating propyl iodide, silver sulphate, and ether in sealed tubes at 130°, is an oil boiling at 120° under 20 mm. pressure, and having a sp. gr. 1.11 at 22.5°; it has an agreeable odour, and is only very slowly decomposed by water.

Diisoamyl sulphate, obtained like the preceding ester, boils at 140—145° under 15 mm., and at 145—155° under 20 mm. pressure; the yield in this case is poor owing to a decomposition resulting in the deposition of coke and the formation of sulphurous acid.

Ethyl chloride, when heated at 625°, either alone or in contact with pumice, is completely decomposed into ethylene and hydrogen chloride, but when passed over soda-lime at 350°, it yields hydrogen, methane, water, and ethyl alcohol, but very little ethylene. This difference is explained by assuming that at the lower temperature the chloride undergoes the alkylidene dissociation into hydrogen chloride and ethylidene, $\text{CH}_3\cdot\text{CH}<$, the former product being fixed by the alkali, whilst the latter is successively oxidised by the same reagent into alcohol and acetic acid. Finally, these substances are also decomposed, yielding hydrogen, methane, water, and a carbonate.

Experiments made on the decomposition of the propyl haloids by alcoholic potassium hydroxide solution and by heat alone confirm the view that propylidene changes into the isomeric olefine even more readily than ethylene. Similar decompositions in the *isobutyl* series are assumed to lead to the formation of *isobutylidene*, an alkylidene capable of changing into any one of the three butylenes. *isoButyl chloride*, when heated at 500° in contact with pumice, dissociates completely into butylene and hydrogen chloride, but the vapours on cooling yield a considerable amount of *tert.*-butyl chloride; a similar result is obtained with *isobutyl bromide*. The three butylenes are formed when these haloids are passed over heated soda-lime, but at temperatures above 600° a certain amount of decomposition occurs, resulting in the formation of hydrogen, methane, and propylene.

The transformation of *isoamylidene* into α - and β -*isoamylenes* is also discussed, and the work of previous investigators on analogous compounds explained on the assumption that in these decompositions an alkylidene is the primary product.

Diethyl sulphate, when heated at 220°, decomposes into ethylidene (2 mols.) and sulphuric acid (1 mol.); about 54 per cent. of the hypothetical hydrocarbon changes into olefine, whilst the remainder interacts with the acid, giving rise to carbon dioxide, sulphur dioxide, water, and carbon. Di-*n*-propyl sulphate decomposes in a similar manner, yielding propylene, &c. *Diisoamyl sulphate* decomposes into trimethylethylene, sulphur dioxide, a tarry product, and a small amount of carbon. Potassium ethyl sulphate, when heated at 250—350°, gives off ethylene, ether, and ethyl alcohol; the *isobutyl* salt gives rise to *isobutyl* alcohol and butylene, and the *isoamyl* salt yields trimethylethylene and *isoamyl* alcohol. In each case, the organic products are accompanied by sulphur dioxide and water. These alkyl sulphates do not furnish olefines when treated with alcoholic potassium hydroxide solution, the sole products under these conditions being the mixed ethers, $\text{C}_n\text{H}_{2n+1}\cdot\text{OEt}$. The results are interpreted by

assuming that the formation of olefine in the decomposition by heat is due to the production of an alkylidene, and the subsequent transformation of this substance into its stable isomeride.

The phenomenon of etherification is assumed to be due to alkylidene dissociation, and the preparation of ether from alcohol by the agency of sulphuric acid and other dehydrating agents is discussed from the standpoint of this hypothesis.

G. T. M.

General Method for Preparing Chlorides of Organic Acids. By HANS MEYER (*Monatsh.*, 1901, 22, 415—442).—The acid is heated with 5—10 times its weight of thionyl chloride, usually at the boiling point of the latter, until completely dissolved; the acid chlorides are generally soluble in the reagent, and can be easily isolated by volatilising the excess of the latter. As only gaseous products (sulphur dioxide and hydrogen chloride) are formed in the action, the method is far preferable to that involving the use of phosphorus pentachloride. *n*-Hexoic, bromoacetic, arachic, and κ -undecenoic acids readily yield their chlorides; *brassic chloride*, $C_{21}H_{41}\cdot COCl$, forms colourless crystals and melts at 14° ; *methyl brassate*, $C_{21}H_{41}\cdot CO_2Me$, crystallises from methyl alcohol in large, lustrous leaflets melting at 34 — 35° . The action of phosphorus trichloride on brassic and erucic acids yields, not the anhydrides as stated by Reimer and Will (*Abstr.*, 1887, 233), but the chlorides of the acids.

Thionyl chloride simply removes the water of crystallisation from oxalic acid, but converts succinic and camphoric acids into the anhydrides; suberic and sebacic acids yield the dichlorides. Maleic, citraconic and itaconic acids give the corresponding anhydrides, but fumaric and mesaconic acids the chlorides. Bromosuccinic acid and malic acid readily yield chlorides, but dibromosuccinic acid is acted on only with difficulty, and then undergoes complex change.

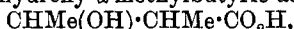
p-Toluic, *o*- and *m*-nitrobenzoic, *o*-chlorobenzoic, *m*-bromobenzoic, phenylacetic, cinnamic, anisic, and veratric acids all readily yield chlorides; from *p*-nitrobenzoic acid a chloride is obtained only with difficulty, and from *p*-bromobenzoic acid not at all. A negative group (NO_2, Br) in the *p*-position thus inhibits the formation of chloride, but a positive group (OMe, Me) has no such influence. *Veratric chloride*, $C_6H_5(OMe)_2\cdot COCl$, forms colourless crystals, melts at 70° , and boils at 275° ; *veratramide* forms colourless crystals and melts at 164° .

The chlorides of aromatic hydroxy-acids, which can be obtained only in exceptional cases by the ordinary methods, are as a rule easily prepared by using thionyl chloride. The *o*- and *m*-hydroxy-acids, salicylic, *m*-hydroxybenzoic, α - and β -cresotic [$CO_2H:Me:OH = 1:2:5$ and $1:2:3$], bromo- β -cresotic acid [$CO_2H:Me:OH:Br = 1:3:2:5$], nitro- β -cresotic and α -resorcylic acids [$CO_2H:(OH)_2 = 1:3:5$] all readily yield chlorides. Only those *p*-hydroxy-acids react, however, which contain a second hydroxyl group in the ortho-position relatively to the first; thus *p*-hydroxybenzoic, β -resorcylic [$CO_2H:(OH)_2 = 1:2:4$], and phloroglucinolcarboxylic acids do not yield chlorides, although protocatechuic, gallic, and pyrogallolcarboxylic acids [$CO_2H:(OH)_3 = 1:2:3:4$] readily do so. Terephthalic acid is not acted on by thionyl chloride, but *isophthalic* acid readily yields a chloride; phthalic acid is

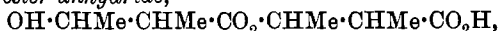
converted into the anhydride. 3-Bromo-4-hydroxy- and 3:5-dibromo-4-hydroxy-benzoic acids readily yield their chlorides, but vanillic acid gives an indefinite product. α -Hydroxynicotinic acid gives a syrupy chloride, but *o*-coumaric acid undergoes complex decomposition; mandelic acid is remarkable in yielding benzaldehyde only.

Methyl m-hydroxybenzoate melts at 57° ; *methyl p-coumarate* crystallises from methyl alcohol in yellow needles melting at 126° , and *methyl l-hydroxynicotinate* from acetone in colourless plates melting at 164° .
W. A. D.

Formation of β -Hydroxy- α -methylbutyric Acid in the Action of Barium Hydroxide on Jalapin. By NICOLAI KROMER (*Arch. Pharm.*, 1901, 239, 373—384).—The product of the action of barium hydroxide on jalapin is acidified, freed from the volatile acids, α -methylbutyric acid, and tiglic acid, by distilling in steam, and then extracted with dry ether, which dissolves two acids. The barium salts of these are separated by alcohol, in which only one is soluble. From the insoluble barium salt, β -hydroxy- α -methylbutyric acid,



is isolated, and from the soluble barium salt a liquid is obtained which consists of a mixture of 1 part of hydroxymethylbutyric acid and 3 parts of the *ester anhydride*,



of β -hydroxy- α -methylbutyric acid. This anhydride, on hydrolysis with potassium hydroxide, yields potassium hydroxymethylbutyrate.

Ethyl β -hydroxy- α -methylbutyrate is a liquid boiling at 176 — 178° . By phosphorus pentachloride it is converted into ethyl tiglate. Hydroxymethylbutyric acid, when heated at 200° or with dilute sulphuric acid, is converted into tiglic acid.

The author believes that α -methylbutyric acid is first formed by the action of barium hydroxide on jalapin; by the further action of barium hydroxide, this is partly converted into hydroxymethylbutyric acid, which in its turn yields tiglic acid.
K. J. P. O.

Purgic Acid. By NICOLAI KROMER (*Arch. Pharm.*, 1901, 239, 389—392. Compare preceding abstract).—Purgic acid, obtained by Hoehnel (*Abstr.*, 1897, i, 228) by the action of barium hydroxide on convolvulin, is shown to be a mixture of β -hydroxy- α -methylbutyric acid and its ester anhydride. The former compound is the main constituent of the mixture.
K. J. P. O.

Glyoxylic Acid. By OSCAR DOEBNER and G. GLASS (*Annalen*, 1901, 317, 147—156. Compare *Abstr.*, 1900, i, 473).—The metallic glyoxylates, with the exception of the ammonium salt, all contain water of crystallisation, and become anhydrous only after continued heating at 105 — 110° . These compounds are most conveniently prepared by neutralising a dilute solution of the acid with the corresponding carbonate, the soluble salts being obtained by evaporation at the ordinary temperature. Their solutions cannot be heated, since, with the exception of the calcium compound, the salts are readily decomposed into the corresponding glycolates and oxalates. *Strontium glyoxylate*, $\text{Sr}(\text{CHO}\cdot\text{CO}_2)_2\cdot 2\text{H}_2\text{O}$, is stable in the air and resembles the

barium salt; the *magnesium* salt, $\text{Mg}(\text{CHO}\cdot\text{CO}_2)_2\cdot 3\text{H}_2\text{O}$, is precipitated by alcohol from its aqueous solution as a white, amorphous, hygroscopic powder. The *aluminium* salt, $\text{Al}(\text{CHO}\cdot\text{CO}_2)_3\cdot \text{H}_2\text{O}$, is crystalline and soluble; the *nickel* and *cobalt* salts, each with $1\text{H}_2\text{O}$, are amorphous substances precipitated from their aqueous solutions by alcohol.

Glyoxythiocarbamide, $\text{CS}\langle\text{N}\cdot\text{CH}\rangle_{\text{NH}}\text{CO}$, obtained by gently heating a mixture of thiocarbamide with a 20 per cent. solution of glyoxylic acid, crystallises from hot water in well-defined, reddish-brown needles and decomposes above 250° ; it is sparingly soluble in organic solvents, but dissolves in aqueous solutions of ammonia or sodium hydroxide, yielding a reddish-yellow solution.

β -Naphthaquinoline-1:3-dicarboxylic acid is produced by adding a mixture of glyoxylic and pyruvic acids to β -naphthylamine dissolved in hot alcohol (compare Doebner and Peters, *Abstr.*, 1890, 1007); this condensation is a characteristic property of aldehydes, and is supplementary evidence in support of the aldehydic nature of glyoxylic acid. The *silver* salt of the dicarboxylic acid is an insoluble, white powder.

G. T. M.

Compounds of Glyoxylic Acid with Guanidine and Amino-guanidine. By OSCAR DOEBNER and SIMON GÄRTNER (*Annalen*, 1901, 317, 157. Compare this vol., i, 261).—The aminoguanidineglyoxylic acid, $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, obtained by the action of glyoxylic acid on aminoguanidine acetate, is identical with the compound prepared by Thiele (*Abstr.*, 1889, i, 7) from chloral and aminoguanidine in aqueous solution, to which he gave the alternative formula, $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$.

G. T. M.

$\beta\beta$ -Dialkylglutaric and γ -Cyano- β -alkylvinylacetic Acids. I. By ICILIO GUARESCHI (*Atti Accad. Sci. Torino*, 1900—1901, 36, 443—458).—The $\beta\beta$ -dialkylglutaric acids may be prepared in practically theoretical yields by hydrolysing the corresponding 3:5-dicyano-2:6-dioxy-4:4-dialkylpiperidines by means of 60 per cent. sulphuric acid, the reaction being: $\text{NH}\langle\text{CO}\cdot\text{CH}(\text{CN})\rangle_{\text{CO}\cdot\text{CH}(\text{CN})}\text{CRR}' + 6\text{H}_2\text{O} = \text{CRR}'(\text{CH}_2\cdot\text{CO}_2\text{H})_2 + 2\text{CO}_2 + 3\text{NH}_3$.

$\beta\beta$ -Dimethylglutaric acid obtained in this way melts at $103\text{--}104^\circ$; former investigators, who prepared the acid in small quantity, or in a state difficult to purify, give lower temperatures for the melting point.

$\beta\beta$ -Methylethylglutaric acid, $\text{CMeEt}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, separates from water in anhydrous, colourless needles soluble in alcohol or ether; it melts at 87° , and boils almost unchanged at about 260° under 740 mm. pressure. The *silver* salt is a white, microcrystalline powder stable towards light and almost insoluble in water; the *zinc* salt forms colourless, greasy plates slightly soluble in water, and the *sodium* salt colourless prisms very soluble in water.

$\beta\beta$ -Methylpropylglutaric acid, $\text{CMePr}^n(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, crystallises from water in colourless needles melting at 92° , and dissolves in alcohol or ether. Its *zinc* salt forms anhydrous, thin plates sparingly soluble in water.

$\beta\beta$ -Methylbutylglutaric acid, $\text{C}_4\text{H}_9\cdot\text{CMe}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, crystallises

from water in colourless plates or prisms which melt at 64—65° and are soluble in alcohol or ether. The *silver* salt is obtained as a white, microcrystalline precipitate stable towards light, and the *zinc* salt as colourless needles or plates almost insoluble in water.

[With EDOARDO PEANO.]— $\beta\beta$ -Diethylglutaric acid, $\text{C}_6\text{H}_{12}\text{O}_4$, separates from water in shining needles which melt at 108°, volatilise unchanged, and dissolve in alcohol or ether.]

$\beta\beta$ -Ethylpropylglutaric acid, $\text{C}_8\text{H}_{16}\text{O}_4$, melts at 71—72°.

The above acids when neutralised with ammonia or with magnesium hydroxide do not undergo decomposition or yield hydrocarbons.

γ -Cyano- β -methyl- β -butenoic acid (γ -cyano- β -methylvinylacetic acid), $\text{CN}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, obtained by the action of 60 per cent. sulphuric acid on 3-cyano-2:6-diketo-4-methyl- Δ^3 -tetrahydropyridine or its ammonium derivative, or on 3:5-dicyano-2:6-diketo-4-methyl- Δ^3 -tetrahydropyridine, crystallises from water in needles or large prisms melting at 199—200°. The aqueous solution gives with ferric chloride a brownish-violet colour, whilst with copper acetate it turns yellow and then deposits orange-yellow crystals; by neutralisation with ammonia and addition of silver nitrate, a yellow precipitate is formed which turns reddish, then brown, and finally black.

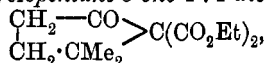
γ -Cyano- β -phenyl- β -butenoic acid (γ -cyano- β -phenylvinylacetic acid), $\text{CN}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, obtained from 3-cyano-4-phenyl-2:6-diketo- Δ^3 -tetrahydropyridine or from 3:5-dicyano-4-phenyl-2:6-diketo- Δ^3 -tetrahydropyridine, melts at 255—256°.

These results show that, under the experimental conditions employed, a secondary cyano-group is readily hydrolysed, whilst a cyano-group in the tertiary state is attacked either only partially or not at all.

T. H. P.

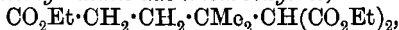
Synthesis of Derivatives of Dimethylcyclopentanone, $\beta\beta$ -Dimethyladipic Acid, and $\alpha\beta\beta$ -Trimethyladipic Acid. By WILLIAM ALBERT NOYES (*J. Amer. Chem. Soc.*, 1901, 23, 392—402).—When heated in sealed tubes with dilute hydrochloric acid, ethyl-2-cyano-3:3-dimethylcyclopentanone-2-carboxylate (Abstr., 1899, i, 929) decomposes into acetic acid, isohexolactone and carbon dioxide, a carbon atom being removed from the ring and replaced by oxygen; in a similar way, hydrolysis with alcoholic potash gives malonic acid and isohexolactone.

Ethyl 2:2-dimethylcyclopentane-5-one-1:1-dicarboxylate,



prepared by condensing ethyl γ -chloroisohexoate (γ -chloro- γ -methylvalerate) with ethyl malonate, is a nearly colourless oil which boils at 167—169° under 14 mm. pressure, and is hydrolysed by alcoholic potassium or sodium hydroxide to malonic and hydroxyisohexoic acids.

Triethyl $\beta\beta$ -dimethylbutane- $\alpha\alpha\delta$ -tricarboxylate,



prepared by condensing ethyl chloroisohexoate with ethyl malonate, boils at 150—172° under 15 mm. pressure. The acid, $\text{C}_9\text{H}_{14}\text{O}_6$, separates from water in compact crystals, melts and decomposes at 165—175° according to the rate of heating, and is only slightly

soluble in cold water. The calcium salt, $\text{Ca}_3(\text{C}_9\text{H}_{11}\text{O}_6)_2 \cdot 5\text{H}_2\text{O}$, is much less soluble in hot than in cold water. $\beta\beta$ -Dimethyladipic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by heating the preceding acid at 200° , crystallises from water in small plates, and melts at 102° ; the melting point is 15° higher than that of the dimethyladipic acids described by Tiemann (Abstr., 1898, i, 377) and by Baeyer (Abstr., 1898, i, 676).

$\alpha\beta\beta$ -Trimethyladipic acid, $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by heating $\alpha\beta\beta$ -trimethylbutane- $\alpha\alpha\delta$ -tricarboxylic acid, crystallises from water or from ether in leaflets, melts at 136° , and appears to exist in two modifications.

Methods are described for the preparation of γ -methylvaleric acid, isohexolactone, and γ -chloro- γ -methylvaleric acid. T. M. L.

Addition of Bromine to Acetylenedicarboxylic Acid. By WILHELM LOSSEN and A. TREIBICH (*Chem. Centr.*, 1901, ii, 191—192; from *Verh. Vers. Deutsch. Naturforsch. Ärzte*, 1900, ii, 1, 92—93).—The amount of acetylenedicarboxylic acid oxidised to carbon dioxide by bromine is greater the larger the quantity of water present, and when a solution of one part of the acid in 50 of water is used, more than half of the bromine acts in this way. When, however, a solution of the acid is treated very slowly with bromine vapour, the halogen combines with the acid to form additive compounds, $\text{C}_4\text{H}_2\text{O}_2\text{Br}_2$, consisting mainly of dibromofumaric acid. E. W. W.

Camphoroxalic Acid Derivatives. VI. By JOHN B. TINGLE (*J. Amer. Chem. Soc.*, 23, 363—391).—A summary is given of previous work on the subject (Trans., 1890, 57, 652; Abstr., 1897, i, 484; 1898, i, 443; 1899, i, 444; 1900, i, 302).

Camphoformeneaminecarboxylic acid, $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{C}:\text{C}(\text{NH}_2) \cdot \text{CO}_2\text{H} \\ \text{CO} \end{smallmatrix}$, prepared by the action of ammonium chloride and potassium hydroxide on a solution in alcohol of camphoroxalic acid, crystallises from benzene or from a mixture of acetone and light petroleum in colourless plates, melts at 178° with liberation of gas, dissolves in sodium carbonate solution only when heated, and is reprecipitated by acids. The amide, prepared in a similar manner from ethyl camphoroxalate, crystallises from xylene in colourless, microscopic needles, melts at 227 — 228° , and appears to give camphoroxalic acid when boiled with aqueous sodium hydroxide; the *platinichloride* crystallises in hexagonal, orange plates. By passing dry ammonia into a solution of ethyl camphoroxalate in ether or absolute alcohol, an additive compound, probably

$\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH} \cdot \text{C}(\text{NH}_2)(\text{OH}) \cdot \text{CO}_2\text{Et} \\ \text{CO} \end{smallmatrix}$, is formed as a white precipitate; it gradually decomposes into its constituents, and, when heated at 100° in a sealed tube with alcoholic ammonia, is converted into the amide described above.

Hydroxylamine acts on ethyl camphoroxalate to form a compound of unknown constitution, which crystallises from a mixture of toluene and light petroleum in colourless, slender needles, and melts at 120 — 121° .

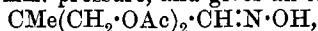
Camphoformenemethylaminocarboxymethylamide crystallises from a mixture of benzene and light petroleum in small, white needles and melts at 130° . *Camphoformeneethylaminocarboxyethylamide* crystallises from benzene in colourless needles and melts at 148° .

Ethyl methylcamphoroxalate, $C_8H_{14} \begin{smallmatrix} & C:C(OMe) \cdot CO_2Et \\ & | \\ & CO \end{smallmatrix}$, prepared by

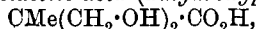
heating ethyl camphoroxalate with silver oxide and methyl iodide, was not obtained in a crystalline form, but the *acid* crystallises from light petroleum in large, hexagonal prisms and plates and melts at $95-96^{\circ}$.

T. M. L.

Condensation of Propaldehyde and Formaldehyde. By HUGO KOCH and THEODOR ZERNER (*Monatsh.*, 1901, 22, 443-459).—*αα-Dimethylolpropaldehyde*, $CMe(CH_2 \cdot OH)_2 \cdot CHO$, obtained by leaving propaldehyde and formaldehyde (2 mols.) with aqueous potassium carbonate for 3-4 days at the ordinary temperature, is a slightly yellow, odourless oil which decomposes when distilled at $70-80^{\circ}$ in a vacuum, and on reduction yields the pentaglycerol, $CMe(CH_2 \cdot OH)_3$ (Hosäus, *Abstr.*, 1893, i, 617). The *oxime* cannot be purified, but, when heated with acetic anhydride for a day, gives the *acetate*, $CN \cdot CMe(CH_2 \cdot OAc)_2$, of *αα-dimethylolpropionitrile*, which boils at $145-147^{\circ}$ under 14 mm. pressure. The *acetate*, $CMe(CH_2 \cdot OAc)_2 \cdot CHO$, of the aldol boils at $170-174^{\circ}$ under 18 mm. pressure, and gives an *oxime*,

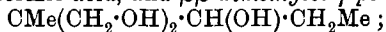


as a thick, colourless liquid boiling at 169° under 19 mm. pressure and yielding the foregoing nitrile when heated with acetic anhydride. When the nitrile is hydrolysed with hydrochloric acid, it gives acetic acid and *methyl dimethylolacetic acid* (*dihydroxypivalic acid*),



which crystallises from ether and melts at $163-164^{\circ}$. Alcoholic potash converts *αα*-dimethylolpropaldehyde into a mixture of this acid and the pentaglycerol, $CMe(CH_2 \cdot OH)_3$, simultaneous oxidation and reduction occurring as in the case of aromatic aldehydes.

Attempts to prepare the aldol, $CHO \cdot CHMe \cdot CH_2 \cdot OH$, by condensing propaldehyde and formaldehyde in molecular proportion gave only *αα*-dimethylolpropaldehyde along with methylethylacraldehyde formed from the excess of propaldehyde. In presence of alcoholic potassium hydroxide, the two aldehydes condense to form the pentaglycerol, $CMe(CH_2 \cdot OH)_3$, formic acid, and *ββ-dimethylol-γ-pentanol*,



this boils at $135-137^{\circ}$ under 15 mm. pressure, and yields a *triacetyl* derivative, $C_{13}H_{22}O_6$, boiling at 136° under 14 mm. pressure.

W. A. D.

Conversion of Pyrrole into the Tetramethylacetal of Succindialdehyde. By CARL D. HARRIES (*Chem. Centr.*, 1901, ii, 307, from *Verh. Vers. Deutsch. Naturforsch. Ärzte*, 1900, ii, 1, 87-89).—Succintetramethylacetal (*Abstr.*, 1898, i, 232) may be obtained by cooling a rather dilute solution of succindialdoxime (*Abstr.*, 1885, 246; 1889, 1208; 1890, 1155) in methyl alcohol containing sufficient hydrogen chloride to form hydroxylamine hydro-

chloride (2 mols.). When the solution is treated with absolute ether, hydroxylamine hydrochloride and salts of other organic bases are precipitated, and the filtrate, after removal of hydrogen chloride by silver oxide and evaporation, yields an oil which contains an imino-ether of the semi-acetal of succinic acid, $\text{CH}(\text{OMe})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{OMe}) \cdot \text{NH}$, and ethylenedi-imino-ether, $\text{C}_2\text{H}_4[\text{C}(\text{OMe}) \cdot \text{NH}]_2$.

Succintetramethylacetal, $\text{C}_2\text{H}_4[\text{CH}(\text{OMe})_2]_2$, obtained by removing the bases contained in the oil by saturating its ethereal solution with hydrogen chloride, is a stable oil, has an odour like that of paraldehyde, boils at $82-84^\circ$ under 14 mm., and at $182-185^\circ$ under the ordinary pressure, and is easily volatile in steam or alcohol or ether vapour. *Succindialdehyde*, prepared by the action of dilute hydrochloric acid on the tetramethylacetal at 80° , is a colourless oil, has an extremely pungent odour resembling that of heptaldehyde, boils at about $62-65^\circ$ under 12 mm. pressure, readily reduces Fehling's solution in the cold, gives the pyrrole reaction with ammonia and acetic acid, and with hydroxylamine hydrochloride forms the dialdoxime.

E. W. W.

Constitution of, and Action of Aqueous Ammonia on, Sodium Cellulose. By EDMUND THIELE (*Chem. Zeit.*, 1901, 25, 610-612).—Various formulæ have been used to express the empirical constitution of the compound formed by the action of concentrated solutions of sodium hydroxide on cellulose (cotton). The action of aqueous ammonia on "mercerised" cotton has been studied by the present author, and from the quantitative results the formula $\text{C}_{12}\text{H}_{20}\text{O}_{10} \cdot 2\text{NaOH}$ is established for the sodium cellulose. Mercerised cotton is not "demerced" by ammonia, as it remains elastic and is apparently converted into a hydrate of cellulose, which differs from the inelastic hydrate obtained by treating mercerised cotton with water.

R. H. P.

Action of Ammonia on Amine Hydrochlorides. By FÉLIX BIDET (*Compt. rend.*, 1901, 133, 238-239).—Dry ammonia is absorbed by dry ethylamine hydrochloride with liberation of the amine and formation of ammonium chloride, the limiting pressure being 340 mm. at 0° , 462 mm. at 9.8° , and 555 mm. at 16.6° . Diethylamine hydrochloride behaves similarly, but the limiting pressures are much higher, being 891 mm. at 0° , 1167 mm. at 9.5° , and 1301 mm. at 13.5° .

C. H. B.

Aliphatic isocyanides and Nitro-compounds. By FELIX KAUFER and CÉSAR POMERANZ (*Monatsh.*, 1901, 22, 492-496).—Dimethyl sulphate interacts vigorously with concentrated aqueous potassium cyanide at 0° , yielding 75 per cent. of acetonitrile and 25 per cent. of the isocyanide. When potassium nitrite is used, 25 per cent. of the product is nitromethane, the rest being methyl nitrite. Under non-dissociating conditions, the action of the potassium salt takes place mostly by addition, and yields an isocyanide or nitro-compound, as in the case of the silver salts; thus, $\text{AgCN} + \text{MeI} = \text{AgCN} \cdot \text{MeI} \rightarrow \text{AgI} + \text{C} \equiv \text{NMe}$. Where dissociation can occur, the ions of the potassium

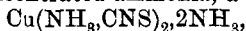
salt are active, and give rise to a nitrile or a nitrite, for example,
 $\text{KCN} + \text{MeI} = \text{KI} + \text{MeCN}.$

W. A. D.

Action of Hypophosphorus Acid on Acetone. By CH. MARIE (*Compt. rend.*, 1901, 133, 219—221).—The prolonged action of glacial hypophosphorus acid on boiling acetone yields a monobasic acid, $\text{C}_6\text{H}_{15}\text{O}_4\text{P}$, which melts and decomposes at 180 — 181° , forms large, lamellar crystals seemingly belonging to the monoclinic system, decomposes carbonates, and yields crystallisable salts. There are formed at the same time, another crystallisable monobasic acid, $\text{C}_3\text{H}_9\text{O}_3\text{P}$, which melts at 40 — 41° , decomposes carbonates, and forms non-crystallisable alkali-salts and a soluble and crystalline lead salt, and a dibasic acid, $\text{C}_3\text{H}_9\text{O}_4\text{P}$, which melts and decomposes at 169 — 170° , and forms an insoluble lead salt.

C. H. B.

Ammonio-compounds of Cupric and Cuprous Thiocyanates. By FRANZ M. LITTERSCHEID (*Arch. Pharm.*, 1901, 239, 336—340. Compare Schmidt and Malmberg, *Abstr.*, 1898, i, 547).—The author prepares ammonio-cupric thiocyanate, $\text{Cu}(\text{NH}_3 \cdot \text{CNS})_2$, by adding ammonium thiocyanate and dilute ammonia to a solution of copper sulphate (compare Meitzendorff, *Ann. Phys. Chem.*, 1842, 56, 85). By use of concentrated solutions, or treatment of the ammonio-cupric compound just mentioned with concentrated ammonia, a compound,



is obtained as lustrous, dark blue, rhombic plates which slowly evolve ammonia.

Cuproso-cupric thiocyanate does not combine with ammonia, but yields ammonio-cupric thiocyanate.

K. J. P. O.

Action of Sunlight on Aqueous Solutions of Potassium Ferrocyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, 25, 565—566. Compare this vol., i, 455 and 584).—Aqueous solutions of potassium ferrocyanide decompose in sunlight according to the equation: $4\text{KCN} \cdot 2\text{Fe}(\text{CN})_2 + 6\text{H}_2\text{O} = \text{Fe}_2(\text{OH})_6 + 6\text{KCN} + 6\text{HCN}.$ The amount of ferric hydroxide formed increases in arithmetical progression as the concentration of the solution decreases.

R. H. P.

Action of Sulphur Dioxide on [Aqueous Solutions of] Potassium Ferrocyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, 25, 612. Compare following abstract).—Berlin blue is formed by the action of sulphur dioxide on aqueous potassium ferrocyanide only in direct sunlight and in the presence of air.

R. H. P.

Action of Sulphur Dioxide on Aqueous Solutions of Potassium Ferricyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, 25, 587—588).—An aqueous solution of potassium ferricyanide in the absence of light is not altered by a stream of sulphur dioxide, but in the presence of light is decomposed with the formation of Berlin blue in accordance with the equation, $7[\text{Fe}_2(\text{CN})_6] + 6\text{KCN} + 21\text{SO}_2 + 24\text{H}_2\text{O} = 2\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 21\text{K}_2\text{SO}_3 + 48\text{HCN} + 3\text{O}$, the hydrogen cyanide in the presence of an excess of sulphur dioxide being converted into formic acid.

R. H. P.

Comparative Experiments on the Intensity of the Action of Light on Aqueous Solutions (containing Equal Amounts of Iron) of Potassium Ferrocyanide and Ferricyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, 25, 601. See this vol., i, 455 and 584).—Aqueous solutions of potassium ferricyanide are decomposed with the formation of ferric hydroxide by light quicker than solutions of potassium ferrocyanide containing the same amount of iron. In the case of the ferricyanide, traces of Berlin blue are formed in amounts which increase with the concentration of the solution and the consequent decrease in the amount of ferric hydroxide formed.

R. H. P.

Additive Reactions of Thiol Acids. By HENRY L. WHEELER [and, in part, BAYARD BARNES and WILLIAM VALENTINE] (*J. Amer. Chem. Soc.*, 1901, 23, 443—449. Compare Abstr., 1900, i, 563, 564, 632, and this vol., i, 514).—Phenylthiocarbimide and thiobenzoic acid readily form an additive product, *benzoylthiolcarbanilic acid*, $\text{NBzPh}\cdot\text{CO}\cdot\text{SH}$, which crystallises in colourless needles melting and decomposing at 97—99°, and on heating is converted into carbonyl sulphide and benzanilide. Diphenylformamidine and thiobenzoic acid form an additive product, $\text{C}_{20}\text{H}_{18}\text{ON}_2\text{S}$, which crystallises in colourless needles, melts at 145—150°, and when heated yields thioformanilide and benzanilide. The additive product, $\text{C}_{20}\text{H}_{18}\text{ON}_2\text{S}$, from phenylbenzenylamidine and thiobenzoic acid, crystallises in yellowish-white needles melting at 141—142°. Phenyl-*p*-tolylbenzenylamidine and the thiol acid yield a compound, $\text{C}_{27}\text{H}_{24}\text{ON}_2\text{S}$, as a yellow precipitate melting at 131—132°. Benzinon-*n*-propyl ether and thiobenzoic acid give a very unstable compound, which, on warming, decomposes into benzamide and *n*-propyl thiolbenzoate, which is an oil boiling at 251—255°.

These additive products are analogous to that formed from benzylideneaniline and thioacetic acid (Eibner, this vol., i, 321). The author believes that the addition of the thiol acid to the group $\text{C}:\text{N}-$ takes place in two different ways. Thus, in the case of thiobenzoic acid and phenyl thiocarbimide, the benzoyl group becomes attached to the nitrogen, and the compound is represented by the formula previously given, whilst with the amidines the additive compound is best represented by the formula $\text{NH}_2\cdot\text{CR}(\text{NH}_2)\cdot\text{SBz}$.

No additive product but only phenylacetamide was obtained from phenylacetiminomethyl ether and thiobenzoic acid. Acetonephenylhydrazine and thiobenzoic acid gave benzoylphenylhydrazine and some dibenzoylphenylhydrazine.

Diisobutylamine thiolbenzoate, $\text{NH}(\text{C}_4\text{H}_9)_2\cdot\text{SHBz}$, prepared from *iso*-butylamine and thiobenzoic acid, crystallises in flattened prisms melting at 124°.

Methyl alcohol reacts with thiobenzoic acid, producing methyl benzoate; the reaction of the acid with phenol is much slower.

K. J. P. O.

Dichlorinated *o*-Xylenes. By LUCIEN FERRAND (*Compt. rend.*, 1901, 133, 169—171).—On passing chlorine into cold *o*-xylene containing 1 per cent. of iodine and 10 per cent. of *m*-xylene as an impurity, a solid, melting at 68.5—72°, and two liquids, boiling respectively at

226—228° and 229—231.5°, are obtained (compare Claus and Kantz, Abstr., 1885, 972; 1890, 1247). The solid is a mixture of 3:4-dichloro-*o*-xylene and dichloro-*m*-xylene; both liquids are mixtures of 4:5- and 3:6-dichloro-*o*-xylenes and dichloro-*m*-xylene. This was established by studying the phthalic acids formed on oxidation with dilute nitric acid; 3:4-dichloro-*o*-phthalic anhydride sublimes in white needles, melts at 185—186°, yields a *phthalimide* melting at 219°, and a *phenylimide* melting at 209°; 3:4-dichloroanthranilic acid melts at 183°.

W. A. D.

Chlorination of *o*-Nitrotoluene. By PAUL COHN (*Monatsh.*, 1901, 22, 473—491).—Under Janson's conditions (Germ. Pat. 107505), the principal product of the chlorination of *o*-nitrotoluene is 6-chloro-2-nitrotoluene, but a considerable amount of the 4-chloro-2-nitro-compound is also formed; this was shown in two ways. (1) The product was oxidised to chloronitrobenzoic acid and esterified; the 6-chloro-2-nitrobenzoic acid, according to V. Meyer's rule, did not yield an ester, but considerable quantities of the isomeric ethyl 4-chloro-2-nitrobenzoate were formed. (2) The chlorination product was reduced to chlorotoluidine, acetylated and oxidised by potassium permanganate; a 4-chloroanthranilic acid was isolated from the product.

6-Chloro-2:3-dinitrotoluene, obtained by the nitration of 6-chloro-2-nitrotoluene with a mixture of nitric and sulphuric acids at 0°, crystallises from alcohol in nearly white, rhombic plates [$a:b:c = 1:0.667:1.05$] and melts at 106°; the relatively ortho-position of the two nitro-groups follows from the fact that no action occurs on boiling the substance with potassium hydroxide or aniline, and that on reduction a *diamine* is formed which crystallises from a mixture of light petroleum and benzene, melts at 46—47°, and combines with dihydroxy-tartaric acid to form an *azine*, $C_6H_2MeCl \begin{smallmatrix} N:C:CO_2H \\ N:C:CO_2H \end{smallmatrix}$, crystallising in slender, white needles, and melting at 201—203°.

Pure 6-chloro-*o*-toluidine boils at 242—244°; its acetyl derivative melts at 157° [Hönig (Abstr., 1887, 1034) gives 136°]; the *hydrochloride* forms silvery, lustrous leaflets, and decomposes at 250—252°; the *sulphate* is similar and decomposes at the same temperature; the *platinichloride*, *nitrate*, and *oxalate* are also described. The *benzoyl* derivative crystallises from alcohol in lustrous needles, and melts at 170—171°.

The structure of 4-chloro-*o*-toluidine (m. p. 140°) was determined by oxidising its acetyl derivative with aqueous potassium permanganate in presence of magnesium sulphate to 4-chloro-2-acetylaminobenzoic acid, $CO_2H \cdot C_6H_3Cl \cdot NHAc$, which crystallises from dilute alcohol in bright brown needles, melts at 235—236°, and yields 2:4-dichlorobenzoic acid through the diazo-reaction.

6-Chloroacetyl-*o*-toluidide, on similar oxidation, yields 6-chloro-2-acetylaminobenzoic acid, which crystallises from water in white, lustrous needles and melts at 215°; 6-chloro-2-aminobenzoic acid, $NH_2 \cdot C_6H_3Cl \cdot CO_2H$, crystallises from benzene in slender, yellowish-white needles, melts at 146—147°, and yields a *hydrochloride* which forms long, white needles and melts and decomposes at 195°. It

is converted by the diazo-reaction into 2:6-dichlorobenzoic acid (m. p. 133—134°).

On reduction with zinc dust and sodium hydroxide, 6-chloro-2-nitrotoluene yields, along with 6-chloro-*o*-toluidine, *oo*-dichloroazotoluene, and *oo*-dichlorotolidine [Cl:Me:NH₂=2:3:4, German Patents 82140 and 97101]; the former crystallises from benzene in orange-red, prismatic needles and melts at 153—154°, the latter softens at 192°, melts at 197°, and yields a crystalline *hydrochloride* and *sulphate*. W. A. D.

Tervalent Carbon. By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1901, 23, 496—502. Compare this vol., i, 77, 198, 374).—When zinc is allowed to act on triphenylchloromethane in the presence of ether (*loc. cit.*), a dark, viscous mass separates, together with white crystals. The former is a compound of triphenylchloromethane and zinc chloride. Using benzene as solvent, the same substance is precipitated; in the presence of ethyl acetate, it is not formed, as it is soluble in this solvent. It is most readily prepared by adding a solution of zinc chloride in ether to a solution of triphenylchloromethane in benzene. This additive compound could not be obtained in a crystalline state, but a number of other crystalline compounds of triphenylchloromethane and metallic chlorides have been prepared, and will be described later.

The white crystals are a *compound* of triphenylmethyl and ether, 2CPh₃.Et₂O, and do not lose ether when kept in an exhausted desiccator over sulphuric acid. The similar crystals obtained when ethyl acetate is the solvent are a *compound* of triphenylmethyl and ethyl acetate, 2CPh₃.CH₃.CO₂Et; this substance is more stable than the ether compound. The author suggests for the ether compound the formula Et₂O:(CPh₃)₂, in which oxygen is quadrivalent. K. J. P. O.

New Method for preparing Aniline and Analogous Bases. By PAUL SABATIER and JEAN BAPTISTE SENDERENS (*Compt. rend.*, 1901, 133, 321—324).—Nitrobenzene is quantitatively transformed into aniline by passing its vapour, mixed with hydrogen, over copper reduced from its oxide and heated at 300—400°. No change in the metal occurs. *o*- and *m*-Nitrotoluenes yield pure toluidines in a similar manner.

Freshly reduced nickel is similar, but more vigorous in its action; at 200°, the action is normal, but at 250°, benzene, cyclohexane, and ammonia, as well as aniline, result from nitrobenzene. At 300°, benzene is the principal product, and if the hydrogen is in great excess methane is also formed; above 300°, in presence of little hydrogen, aniline, benzene, ammonia, and diphenylamine are produced, the last-named base being formed by the action of the nickel on the aniline.

Iron, reduced from its oxide at 450—500°, and cobalt act like nickel; platinum black is very similar in its action to copper, no ammonia being formed, but in presence of little hydrogen some hydrazobenzene is produced.

Water-gas can be used instead of hydrogen with copper at 300—400°, and nickel at 200—230°, and the same is true of coal gas purified by passage over heated copper turnings. W. A. D.

Limits of Combination in Tertiary Amines. By EDGAR WEDEKIND (*Annalen*, 1901, 318, 90—116. Compare Abstr., 1900, i, 155, and this vol., i, 216).—On treating dimethylaniline with a series of alkyl iodides, it is found that the yield of quaternary iodide rapidly diminishes as the homologous series is ascended, the proportions of the compounds NMe_2PhI and NMe_2EtPhI obtained being 89 and 16 per cent. respectively. Methyl iodide and benzyl iodide have similar capacities for addition, the yield of quaternary salt from the latter compound being 83 per cent. The substitution of a branched chain derivative for its normal isomeride greatly diminishes the capacity for combination, the yield of *n*-propyl salt being 28 per cent., whilst that of the *isopropyl* compound is only about 5; a similar result is observed in the case of the butyl quaternary iodides. Allyl iodide is the most reactive of the haloether compounds under investigation, the yield of the compound $\text{C}_3\text{H}_5\cdot\text{NMe}_2\text{PhI}$ being about 93 per cent.

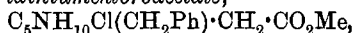
The facility with which any given quaternary iodide may be prepared depends entirely on the order in which the radicals are introduced; thus, only a 15 per cent. yield of the salt NMe_2EtPhI is obtained by treating dimethylaniline with ethyl iodide, whereas the reaction between ethylmethylaniline and methyl iodide is quantitative. Methyl iodide reacts with *diisopropyl*- and *diisoamyl*-anilines, giving yields of about 45 per cent. *iso*Propyl and *iso*amyl iodides, on the other hand, exhibit very little tendency to combine with dimethylaniline, the yield in each case being less than 3 per cent. Any asymmetric quaternary iodides may be formed from the corresponding tertiary bases in three different ways, each mode of combination having a different velocity of reaction. Ethylallylaniline readily combines with benzyl iodide to yield the quaternary salt, $\text{CH}_2\text{Ph}\cdot\text{NEtPhI}\cdot\text{C}_2\text{H}_5$, but does not react with benzyl bromide, so that the iodide just falls within the limits of the base's capacity for combination.

Although triethylamine forms a dibromide, it is not possible to obtain compounds of the type $\text{NEt}_3\text{Cl}\cdot\text{CO}\cdot\text{R}$ by treating this base with an acid chloride.

When triethylamine is treated with benzoyl or acetyl chloride, the hydrochloride of the tertiary base is produced, and in the latter experiment dehydracetic acid is simultaneously formed in accordance with the following equation, $4\text{AcCl} + 4\text{NEt}_3 = 4\text{NEt}_3\cdot\text{HCl} + \text{C}_8\text{H}_8\text{O}_4$; triethylamine hydrochloride is also formed by the action of phenylacetyl chloride on the tertiary base. Benzylpiperidine reacts with ethyl chlorocarbonate, and triethylamine and other tertiary bases yield crystallisable additive compounds with the alkyl esters of the haloether acetates.

Methyl triethylammoniumiodoacetate, $\text{NEt}_3\text{I}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, prepared by mixing triethylamine with methyl iodoacetate at the ordinary temperature, crystallises from acetone in lustrous, monoclinic prisms, and melts and decomposes at 138—139°.

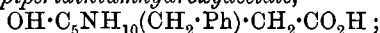
Ethyl benzylpiperidiniumchloroacetate,



obtained by warming benzylpiperidine and methyl chloroacetate for 4 hours on the water-bath, crystallises from chloroform or benzene in colourless needles and melts at 193—194°. The corresponding *bromo*-

acetate is produced either by heating together benzylpiperidine and ethyl bromoacetate, or by adding benzyl bromide to ethyl piperidylacetate; it melts and decomposes at 133—134°. *iso*Propylpiperidine and ethyl bromoacetate also yield a crystalline, additive product.

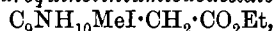
Methyl quinoliniumiodoacetate, $C_9NH_7I \cdot CH_2 \cdot CO_2Me$, produced by mixing its generators at the ordinary temperature, crystallises from alcohol in reddish-brown needles and decomposes at 151—152°. On treating an aqueous solution of methyl benzylpiperidiniumiodoacetate with silver oxide, a small quantity of a compound is produced which is probably *benzylpiperidiniumhydroxyacetate*,



it crystallises in rhombic prisms.

Dimethylaniline and ethyl iodoacetate combine, yielding *ethyl phenyldimethylammoniumiodoacetate*, a compound crystallising in silvery leaflets and melting at 126—127°; diethylaniline under these conditions yields only a tarry product.

Methyl methyltetrahydroquinoliniumiodoacetate,



obtained from kairolin and ethyl iodoacetate, crystallises from acetone in yellowish, monoclinic prisms and melts at 118—119°; it is accompanied by an isomeride separating in rhombohedral crystals and melting at 167—169°. The former compound is the normal product, and can be produced by the addition of methyl iodide to *ethyl tetrahydroquinolylacetate*, $C_9H_{10}N \cdot CH_2 \cdot CO_2Et$; the latter substance is prepared by heating tetrahydroquinoline with ethyl chloroacetate on the water-bath; it is an oil boiling at 180—190° under 17 mm. pressure, and having decidedly basic properties.

Kairolin, when treated with methyl iodoacetate, yields two products, melting respectively at 150—155° and 164—166°. The substance of lower melting point is the normal *methyl tetrahydroquinoliniumiodoacetate*; it is also prepared by the action of methyl iodide on *methyl tetrahydroquinolylacetate*, an oil boiling at 170—190° under 13 mm. pressure, prepared by the action of ethyl chloroacetate on tetrahydroquinoline. The nature of the by-products obtained by the action of alkyl iodoacetates on kairolin has not been determined.

G. T. M.

The Supposed Existence of Miller and Plöchl's Stereoisomeric Anil Compounds [Constitution of Eckstein's Ethylideneaniline]. By ALEXANDER EIBNER (*Annalen*, 1901, 318, 58—89. Compare Abstr., 1899, i, 41).—Ethylideneaniline (m. p. 126°), the stable base obtained by the condensation of aniline and acetaldehyde (Eckstein, Abstr., 1892, 1191), is now considered to have the structural

formula $NHPh \cdot CHMe \cdot \overset{|}{CH}$ and the following experimental data

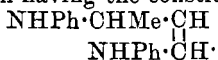
confirm this view of its constitution.

The *hydrochloride*, $C_{16}H_{18}N_2 \cdot 2HCl$, and the *nitrate*, $C_{16}H_{18}N_2 \cdot 2HNO_3$, are stable, colourless salts, crystallising respectively in lustrous prisms and aggregates of needles. The *diacetyl* derivative crystallises from alcohol in highly refractive prisms and melts at 188°. The monobenzoyl derivative yields the *nitrosoamine*, $C_{23}H_{21}O_2N_3$, on treatment

with nitrous acid; this product crystallises from ether in amber-coloured prisms and melts at 147.5° . The nitrosoamine gives Liebermann's reaction, and when treated at the ordinary temperature with alcoholic hydrochloric acid becomes transformed into the isomeric *nitroso*-compound; this substance closely resembles nitrosodimethylaniline and melts at 217° . Eckstein's base is not reduced by sodium and amyl alcohol, and does not combine with hydrogen cyanide. These results all point to the existence of two aniline residues (NHPH-) in the compound.

The existence of the olefine linking is demonstrated by the behaviour of the monobenzoyl derivative towards bromine; this compound readily takes up 1 mol. of bromine in chloroform solution, and yields the *dibromide*, $C_{23}H_{22}ON_2Br_2$, a substance crystallising in lustrous leaflets and melting at 218° . Two products melting respectively at 179.5° , and 156° , are obtained by the action of bromine on the diacetyl compound, but these substances are still under investigation.

The labile isomeride of Eckstein's base (m. p. 85°), discovered by Eibner (Miller and Plöchl, Abstr., 1894, i, 410), is considered to be a stereoisomeric modification having the constitution



Both substances yield benzylidenequinaldine and benzyaniline when heated with benzaldehyde, but the reaction takes place more readily in the case of the *cis*-modification.

The *trans*-base may be distilled without decomposition, whereas the *cis*-isomeride, on heating, decomposes into quinaldine, aniline, and hydrogen; moreover, it is readily converted into the stable compound by the action of a trace of iodine. The stable base may also be prepared either by condensing aniline (2 mols.) with aldol or paralldol, or by warming aldol-aniline with a further quantity of the base.

The higher homologues of Eckstein's base yield *dinitrosoamines* with very dilute alcoholic solutions of nitrous acid, that from Wormser's base, ethylidene-*p*-toluidine (m. p. 116°), crystallises in yellow needles and melts at 156° , and the corresponding derivative of Sender's base, propylideneaniline (m. p. 103°), forms yellow prisms melting at 135° .

The base obtained from acetaldehyde and *as-m*-xylylidine (Mozdzynski Abstr., 1895, i, 534) yields a pale yellow, amorphous *nitrosoamine*.

G. T. M.

Condensation of *iso*Butaldol with Aniline. By ERNST FRIEDJUNG and GUSTAV MOSSLER (*Monatsh.*, 1901, 22, 460—472).—The condensation of *isobutaldol* with aniline in presence of a saturated potassium carbonate solution gives a mixture of the *dianil*, $\text{CHPr}^{\beta}(\text{NHPH})_2$, of *isobutaldehyde* and the *anil*, $\text{OH} \cdot \text{CHPr}^{\beta} \cdot \text{CMe}_2 \cdot \text{CH} \cdot \text{NPh}$, of the aldol. The former boils at 86 — 87° under 18 mm. pressure, is slowly oxidised in the air to hydrazobenzene and *isobutaldehyde*, and by alkaline potassium permanganate to azobenzene and *isobutyric acid*; the latter boils at 106 — 109° under 18 mm. pressure, and is resolved by warm dilute mineral acids into aniline and the aldehyde, instead of yielding a quinoline derivative.

The action of aniline on *isobutaldehyde* (compare Miller, Plöchl, and Lettenmayer, Abstr., 1892, 1192) yields a mixture of the dianil,

$\text{CHPr}^s(\text{NHPh})_2$, and the *anil*, CHPr^sNPh , which boils at 95° under 18 mm. pressure; a considerable quantity of hydrazobenzene is also formed.

W. A. D.

New Diphenylamine Derivatives. By PAUL COHN (*Monatsh.*, 1901, 22, 385—397).—The dinitrochlorobenzoic acid of the German Patent 106510 yields 3:5-dinitro-2-aminobenzoic acid when boiled with an excess of aqueous ammonia, and 3:5-dinitrosalicylic acid when heated with aqueous sodium hydroxide for 6 hours; its structure is therefore $\text{CO}_2\text{H}:\text{Cl}:(\text{NO}_2)_2 = 1:2:3:5$. The *ethyl* ester crystallises from light petroleum in long, yellowish plates and melts at 54° .

The following compounds were obtained by condensing the acid with various bases. 2:4-Dinitrodiphenylamine-6-carboxylic acid, prepared by using aniline, crystallises from dilute alcohol in yellow needles and melts at 214° ; the *sodium* salt forms dark yellow, and the *potassium* salt red needles, the *calcium* salt orange-yellow, and the *barium* salt yellow plates; the *ammonium* salt is monoclinic

$$[a:b:c = 1.9337:1:1.9227; \beta = 107^\circ.67'].$$

The *acetyl* derivative forms yellow needles and melts at $209\text{--}210^\circ$; the *benzoyl* derivative is microcrystalline and melts at $120\text{--}121^\circ$.

1:3-Dinitroacridone, $\text{C}_6\text{H}_2(\text{NO}_2)_2 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$, obtained by heating the acid with concentrated sulphuric acid for 5 hours at 100° , crystallises from pyridine in lustrous scales and does not melt at 300° .

2:4-Dinitro-4'-hydroxydiphenylamine-6-carboxylic acid, obtained by using *p*-aminophenol (German Patent 108872), forms lustrous, dark red needles, melts at 103° , and yields a red, microcrystalline, *sodium* salt; the *potassium* salt forms stellate aggregates of red needles, and the *ammonium* salt, red, six-sided plates; the *barium* salt is deliquescent. The *acetyl* derivative crystallises from water in red needles melting at $97\text{--}99^\circ$, and the *benzoyl* derivative in yellow needles melting at 123° .

2:4-Dinitrophenyl α -naphthylamine-6-carboxylic acid, obtained by using α -naphthylamine, crystallises from dilute alcohol in lustrous, red needles, and melts at $150\text{--}151^\circ$; the *sodium* and *potassium* salts form orange-red needles, and the *ammonium* salt is microcrystalline. The *acetyl* derivative is easily soluble in alcohol, and the *benzoyl* derivative crystallises in small, red needles.

2:4-Dinitrophenyl β -naphthylamine-6-carboxylic acid crystallises from dilute alcohol in microscopic, orange-red needles and melts at $238\text{--}239^\circ$; the *sodium* and *potassium* salts crystallise in orange-red plates, and the *ammonium* salt in lustrous, red, four-sided plates. The *acetyl* derivative is very soluble in alcohol, whilst the *benzoyl* derivative crystallises in lustrous, orange-yellow needles, melting above 300° .

2:4-Dinitrodiphenylamine-6:6'-dicarboxylic acid, obtained by using anthranilic acid, crystallises from dilute alcohol in yellowish-brown, lustrous needles, sinters at 135° and melts between 153° and 159° . The *alkali* salts are very soluble in water, the *calcium* salt is a crystalline precipitate, and the *barium* salt forms small, orange needles. The *acetyl* derivative forms small, yellow needles and melts at $254\text{--}255^\circ$.

W. A. D.

Phenacylphenacetin. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1901, 25, 628).—*Phenacylphenacetin*, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{Nac} \cdot \text{CH}_2 \cdot \text{COPh}$, obtained by the action of bromoacetophenone on sodium phenacetin, is a crystalline substance melting at 87° , is soluble in alcohol and glycerol but insoluble in water, is not poisonous, and acts as a hypnotic antipyretic.

Triphenylguanidine guaiacolsulphonate, obtained by the action of triphenylguanidine sulphate on barium guaiacolsulphonate, crystallises in leaflets, melts at 50° and can be used as a local anæsthetic.

R. H. P.

[Ethers and Esters of 2:4-Di-iodo- and 2:4:6-Tri-iodophenol.] By P. BRENANS (*Compt. rend.*, 1901, 133, 160—162).—The following ethers were prepared from 2:4-di-iodo- and 2:4:6-tri-iodophenol by heating them with the alkyl iodide and alcoholic potassium hydroxide, and the esters by interaction with the acid chlorides.

From 2:4-di-iodophenol:—The *propyl* ether crystallises from benzene in lamellæ melting at 32° , the *isopropyl* ether boils at $235\text{—}237^\circ$ (corr.) under 77 mm. pressure, and the *allyl* ether at $110\text{—}112^\circ$ under 139 mm. pressure. The *benzoate* crystallises from acetic acid and light petroleum in slender, flattened needles and melts at $96\text{—}97^\circ$; the *succinate* forms prisms melting at 209° , and the *phthalate* needles melting at 153° .

From 2:4:6-tri-iodophenol:—The *methyl* ether crystallises from light petroleum in colourless spangles, from ether in long needles, and melts at $98\text{—}99^\circ$; the *ethyl* ether forms long, colourless needles melting at 83° ; the *propyl*, *allyl*, and *benzyl* ethers separate in needles and melt respectively at 81° , $113\text{—}114^\circ$, and 123° . The *acetate* crystallises from light petroleum in needles or triclinic prisms melting at 156° ; the *benzoate* crystallises from benzene in large prisms and melts at 137° .

W. A. D.

Pyrogallolsulphonic Acids. By MARCEL DELAGE (*Compt. rend.*, 1901, 133, 297—299. Compare *Abstr.*, 1900, i, 595, and this vol., i, 274).—When phenolphthalein is used as indicator, pyrogallolmonosulphonic acid reacts as a dibasic acid and the disulphonic acid as a tribasic acid, owing to the acidic function of one of the OH groups.

Potassium pyrogallolsulphonate, $\text{C}_6\text{H}_3\text{O}_3 \cdot \text{SO}_3\text{K} \cdot 2\text{H}_2\text{O}$, forms large, transparent crystals readily soluble in water; the *sodium* salt, with $2\text{H}_2\text{O}$, and the *ammonium* salt, with $1\text{H}_2\text{O}$, crystallise in colourless prisms and needles.

Potassium pyrogalloldisulphonate, $\text{C}_6\text{H}_4\text{O}_3(\text{SO}_3\text{K})_2 \cdot 2\text{H}_2\text{O}$; the *sodium* salt, with $3\frac{1}{2}\text{H}_2\text{O}$, and the *ammonium* salt, with $2\text{H}_2\text{O}$, are crystalline and readily soluble in water; the *aluminium* and *magnesium* salts form small needles slightly yellow in colour.

J. J. S.

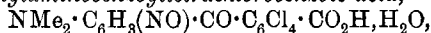
Action of Hydrobromic and Hydrochloric Acids on the so-called Dinaphthylene Glycol. By R. FOSSE (*Compt. rend.*, 1901, 133, 236—237).—The compound obtained by the action of hydrobromic acid at 100° on the so-called dinaphthylene glycol can be obtained free from hydrogen bromide and water by crystallising it from hot glacial acetic acid, and it then has the composition $\text{C}_{21}\text{H}_{13}\text{OBr}$, melts

at 218—220°, and is identical with bromodinaphthoxanthene. When boiled with alcohol, it yields dinaphthoxanthene, hydrogen bromide, and aldehyde. The product formed by the action of hydrochloric acid on the so-called glycol is identical with chlorodinaphthoxanthene and resembles the bromo-derivative in its properties. C. H. B.

Action of Benzoyl Chloride on Trioxymethylene in presence of Zinc Chlorine. By MARCEL DESCUDÉ (*Compt. rend.*, 1901, 133, 371—373).—The substance to which the formula $C_{14}H_{12}O_4$ was ascribed (this vol., i, 504) is *methylene dibenzoate*, $CH_2(OBz)_2$, and can also be obtained by the action of benzoic anhydride on trioxymethylene in presence of zinc chloride; it forms large, colourless, monoclinic crystals, melts at 99°, boils and slightly decomposes at 255°, and has a sp. gr. 1.275 at 22°. Its solubility in 100 parts of solvent at 24° is: absolute alcohol, 2.5; ether, 8; acetone, 18; and benzene, 27.

W. A. D.

Derivatives of Dialkylaminobenzoyltetrachlorobenzoic and Dialkylamino-*m*-hydroxybenzoyltetrachlorobenzoic Acids. Corresponding Dialkylaminoanthraquinones and Dialkylamino-hydroxyanthraquinones. By ALBIN HALLER and HERM. UMBGROVE (*Bull. Soc. Chim.*, 1901, [iii], 25, 745—749. Compare this vol., i, 469).—*Nitrosodimethylaminobenzoyltetrachlorobenzoic acid*,



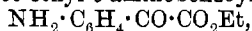
obtained by the action of nitrous acid on dimethylaminobenzoyltetrachlorobenzoic acid, crystallises in yellow scales melting at 129—130°; it loses its water of crystallisation at 110°, and then melts at 145°. *Nitrodimethylaminobenzoyltetrachlorobenzoic acid*, prepared by the action of fuming nitric acid on dimethylaminobenzoyltetrachlorobenzoic acid in acetic acid solution, crystallises in yellow scales melting at 147°.

*Diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid*, obtained by the action of diethyl-*m*-aminophenol on tetrachlorophthalic anhydride, forms colourless crystals melting at 198°; when heated in sulphuric acid solution with dimethyl-*m*-aminophenol, it gives rise to *dimethyldiethyltetrachlororhodamine*, which forms violet-bronze crystals. *Diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid*, obtained by reducing the corresponding benzoyl derivative with zinc and hydrochloric acid, forms small, white crystals melting at 205°.

3-Diethylamino-5:6:7:8-tetrachloroanthraquinone, prepared by the condensation of diethylaminobenzoyltetrachlorobenzoic acid by means of sulphuric acid, crystallises in dark red needles melting at 144°.

3-Diethylamino-1-hydroxy-5:6:7:8-tetrachloroanthraquinone, obtained in an analogous manner from the *m*-hydroxy-acid, crystallises in violet-bronze scales melting at 192°. N. L.

Esters of Anthranilic Acid. By HANS MEHNER (*J. pr. Chem.*, 1901, [ii], 64, 70—85. Compare this vol., i, 470).—The author shows that the solid substance obtained by Erdmann (this vol., i, 536) by the condensation of ethyl formate and methyl *o*-aminobenzoate in the presence of sodium is not ethyl *o*-aminobenzoylformate,



but *ethyl o*-formylaminobenzoate, $HCO \cdot NH \cdot C_6H_4 \cdot CO_2Et$. It can also

be prepared by heating formic acid with ethyl *o*-aminobenzoate at 125—130°. When heated with phosphoric oxide, it gives the odour of *isonitriles*. It crystallises from petroleum in colourless needles or prisms, melts at 57° (Erdmann gives m. p. 49°), and does not form a hydrazone or acetyl derivative. When treated with sodium nitrite and hydrochloric acid, it slowly passes into solution with the formation of *o*-carboethoxybenzenediazonium chloride, $\text{N}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, and elimination of the formyl group. With aniline, this diazonium salt gives *ethyl o*-diazaminobenzoate, $\text{N}_3\text{HPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, which crystallises in yellow needles, melts at 76°, is also obtained from aniline and diazotised ethyl *o*-aminobenzoate, and when boiled with dilute alcohol yields 3-phenylphentriazone.

The oil which Erdmann obtained, together with the solid, contains no ethyl *o*-aminobenzoylformate, but consists mainly of methyl *o*-formylaminobenzoate, as on diazotising and treating with aniline, methyl *o*-diazaminobenzoate (m. p. 71°) is formed. *Methyl o*-formylaminobenzoate, $\text{HCO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, prepared by heating methyl *o*-aminobenzoate and formic acid at 130°, crystallises in aggregates of needles melting at 54°, and when heated with phosphoric oxide gives the odour of *isonitriles*. The *formate* of methyl *o*-aminobenzoate is produced when the ester and formic acid are heated at 100°, and crystallises in white needles melting at 58°.

Ethyl o-acetylaminobenzoate, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, prepared from ethyl *o*-aminobenzoate and acetic anhydride, crystallises in colourless needles or prisms melting at 64—65°; the *benzoyl* derivative crystallises in colourless needles melting at 98°.

Methyl o-benzoylaminobenzoate, $\text{NHBz}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, forms colourless needles melting at 100°. K. J. P. O.

Lobaric and Usnetic Acids. By OSWALD HESSE (*J. pr. Chem.*, 1901, [ii], 64, 110—112. Compare this vol., i, 149).—The author demonstrates that Zopf's suggestion (*Abstr.*, 1897, i, 436) that lobaric acid is merely impure usnetic acid is incorrect. Lobaric acid is a definite chemical substance. K. J. P. O.

Condensation of *iso*Butaldehyde with *p* Hydroxy- and *p*-Ethoxybenzaldehydes. By ARNOLD HILDESHEIMER (*Monatsh.*, 1901, 22, 497—504).—No condensation occurs between *p* hydroxybenzaldehyde and *isobutaldehyde* in alcoholic solution to which concentrated aqueous potassium carbonate has been added; when alcoholic potassium hydroxide is used, the *p*-hydroxybenzaldehyde is recovered unchanged, but the *isobutaldehyde* is converted into *isobutyric acid* and $\beta\beta$ -trimethyl- $\alpha\gamma$ -pentanediol. In presence of aqueous potassium carbonate, *p*-ethoxybenzaldehyde and *isobutaldehyde* yield the *aldol*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CHO}$, which crystallises from alcohol on adding water, and melts at 66—67°; it does not yield an oxime or an acetate, but on reduction with sodium amalgam gives α -*p*-ethoxyphenyl- $\beta\beta$ -dimethyl- $\alpha\gamma$ -propanediol, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$, which melts at 75°, boils at 220—222° under 24 mm. pressure, and is also obtained, along with *isobutyric acid*, by the direct condensation of *p*-ethoxybenzaldehyde and *isobutaldehyde* in presence of alcoholic

potassium hydroxide; the *diacetate*, $C_{17}H_{24}O_6$, of the glycol crystallises from alcohol in colourless, well-formed plates and melts at 70° .

W. A. D.

Electrolytic Reduction of *o*-Nitroanthraquinone in Alkaline, and of 1:5- and α -Dinitroanthraquinone in Acid Solution. By JOHANN MÖLLER (*Zeit. Elektrochem.*, 1901, 7, 797—800).—*o*-Nitroanthraquinone may be reduced to the corresponding amino-compound in slightly alkaline solution by the method of Elbs and Kopp (*Abstr.*, 1899, i, 270). The product is purer than that obtained by the reduction in acid solution (this vol., i, 598).

1:5-Dinitroanthraquinone dissolved in glacial acetic acid containing some sulphuric acid is reduced at 100° by a current of 0.011 ampere per sq. cm. to diaminoanthraquinone. Platinum electrodes were used. The yield is small, the principal product being a compound which dissolves in aqueous sodium hydroxide to a blue solution.

α -Dinitroanthraquinone (m. p. $258-263^\circ$), reduced under the same conditions as the preceding, gave very similar results, the principal product being a colouring matter which dissolved in sodium hydroxide solution to a blue liquid. A small yield of α -diaminoanthraquinone was also obtained.

T. E.

Artificial Camphor and Camphene. By IWAN L. KONDAKOFF (*Chem. Zeit.*, 1901, 25, 609—610).—A discussion of the various views held as to the constitution of artificial camphor, and the relation between it and camphene hydriodide (Kondakoff and Lutschinin, this vol., i, 282).

R. H. P.

Apiin and Apiose. By EDUARD VONGERICHTEN (*Annalen*, 1901, 318, 121—136. Compare this vol., i, 40).—*Apiose*, a new pentose, obtained by hydrolysing apiin, $C_{26}H_{28}O_{14}$, with $\frac{1}{2}$ —1 per cent. sulphuric acid, is isolated in the form of a light yellow syrup. It is slightly dextrorotatory and fermentable, but these properties may be due to traces of dextrose. The *osazone* crystallises in yellow needles; its melting point is indefinite, the substance softening at 145° and melting at 155° . *Apiose-p-bromophenylosazone*, prepared from *p*-bromophenyldiazine and the pentose, crystallises in rosettes of yellow needles and melts at $211-212^\circ$. These derivatives readily dissolve in alcohol, but are much less soluble in water. Apiose behaves quite unlike arabinose and rhamnose when treated with Tollens' phloroglucinol reagent (*Abstr.*, 1892, 290); the latter pentoses yield red and yellow colorations respectively, whilst the new sugar gives a thick, brown, amorphous precipitate; it also differs from the ordinary pentoses in not furnishing furfuraldehyde on distillation with hydrochloric acid.

Apigenin or apiin, when hydrolysed with concentrated sodium hydroxide solution, yields *p*-hydroxyacetophenone, phloroglucinol, and carbon dioxide. The sugar residue of the apiin molecule does not appear to undergo hydrolysis under these conditions, for the alkaline solution, after neutralisation, does not react with Fehling's solution until it has been boiled with hydrochloric acid.

Apiin, when boiled for 5 hours with 25 per cent. sodium hydroxide

solution, becomes hydrolysed into *p* hydroxyacetophenone and *apiosedextrosephloroglucinol*, $C_{11}H_{19}O_9 \cdot O \cdot C_6H_3(OH)_2$; the latter product, obtained in the form of a reddish-brown syrup, gives a slight reduction with Fehling's solution, and is hydrolysed into phloroglucinol, apiose, and dextrose; these compounds, however, interact, yielding a brown, amorphous substance.

A dilute solution of *apiosedextrosephloroglucinol*, treated with benzenediazonium chloride in the presence of sodium carbonate, yields a red *azo*-compound which, when crystallised from alcohol, has the composition $C_{29}H_{32}O_{12}N_4$. This compound is insoluble in cold sodium carbonate solution, but dissolves on warming, and is reprecipitated on cooling or by the addition of a mineral acid. The solution obtained by boiling the *azo*-derivative with dilute sulphuric acid reduces Fehling's solution.

Apiin and *apiosedextrosephloroglucinol* are not hydrolysed by emulsin, yeast, or Fischer's yeast extract (Abstr., 1895, ii, 322). *Dextroseapigenin*, on the other hand, is readily decomposed by emulsin, yielding *apigenin* and *dextrose*.

Apiin is laevorotatory in alkaline solutions, a 6 per cent. solution containing 1 mol. of sodium hydroxide having a rotation of -120° ; the further addition of alkali changes the colour of the solution from dark yellow to pale yellow, and increases the rotatory power by 1° to 1.5° .

G. T. M.

Acetyl Derivatives of Jalapin and Jalapic Acid. By NICOLAI KROMER (*Arch. Pharm.*, 1901, 239, 384—388).—*Pentacetyljalapin* (jalapin pentacetate), $C_{34}H_{58}O_{20}(C_5H_9O)_3Ac_5$, prepared by heating jalapin at 135° with acetic anhydride and sodium acetate, forms a yellow, amorphous powder resembling jalapin. *Decacetyljalapic acid*, $C_{34}H_{56}O_{26}Ac_{10}$, forms a pale yellow, amorphous mass.

K. J. P. O.

Nature and Origin of the Poison of Lotus Arabicus. By WYNDHAM R. DUNSTAN and THOMAS A. HENRY (*Proc. Roy. Soc.*, 1901, 68, 374—378. Compare this vol., i, 39—40).—*Lotusin* has the formula $C_{28}H_{31}O_{16}N$ instead of $C_{22}H_{19}O_{10}N$, which was provisionally assigned to it. It is readily hydrolysed by dilute hydrochloric acid, with formation of *dextrose* (2 mols.), *hydrogen cyanide* (1 mol.), and *lotoflavin* (1 mol.). When warmed with aqueous alkalis, it is gradually decomposed with production of ammonia and *lotusinic acid*.

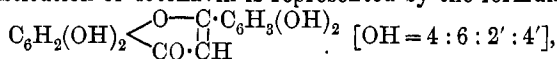
Lotusinic acid, $C_{28}H_{32}O_{16}$, is monobasic, and furnishes yellow, crystalline salts; it is readily hydrolysed by dilute acids with formation of *lotoflavin*, *dextrose*, and *heptogluconic acid*.

Lotoflavin is readily soluble in alcohol or hot glacial acetic acid; it yields a *tetracetyl* derivative, and two isomeric, mutually convertible, *trimethyl* ethers which furnish the same *acetyltrimethylotoflavin*. By the action of fused potassium hydroxide, *lotoflavin* is converted into *phloroglucinol* and β -resorcylic acid.

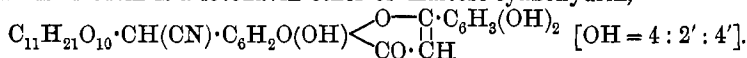
Determination of the amount of *hydrogen cyanide*, yielded by *Lotus arabicus* at different stages of its growth has shown that the maximum of *lotusin* occurs in mature plants bearing seed-pods and flowers.

Lotase resembles emulsin, but has only a feeble effect on amygdalin, and is much more readily deprived of its hydrolytic power by the action of heat or alcohol.

The constitution of lotoflavin is represented by the formula



whilst lotusin is a lotoflavin ether of maltose-cyanohydrin,



The position assigned to the cyanogen group is supported by the fact that mandelonitrile, lævulose cyanohydrin, and pentacetylgluconitrile are, like lotusin, easily decomposed by dilute hydrochloric acid with formation of hydrogen cyanide and the corresponding aldehyde or ketone.

E. G.

Saponins and their Distribution. By LUDWIG WEIL (*Arch. Pharm.*, 1901, 239, 363—373).—The amounts of saponin and saponic acid have been estimated in a number of plants. The ripe seeds of *Camellia theifera*, Griff, contain 0.5 per cent. theosaponic acid and 10 per cent. theosaponin, $\text{C}_{18}\text{H}_{28}\text{O}_{10}$, the roots and the twigs respectively 4 and 2.5 per cent. of this saponin. The dried seeds of *Aesculus Hippocastanum* yield 10 per cent. of the saponin $\text{C}_{16}\text{H}_{24}\text{O}_{10}$. From the soft parts of the dried berries of *Sapindus Mukorossi*, 10.5 per cent. of the saponin, $\text{C}_{17}\text{H}_{26}\text{O}_{10}$, is obtained. In the same part of the plant, *Acacia concinna* contains 5 per cent., and *A. concinna* var. *rugata* 4 per cent., of the saponin $\text{C}_{20}\text{H}_{32}\text{O}_{10}$, *Balanites Roxburghii* contains in the soft parts of the fruit 7 per cent. of the saponin $\text{C}_{18}\text{H}_{28}\text{O}_{10}$. *Illipe latifolia* contains 9.5 per cent. of the saponin $\text{C}_{17}\text{H}_{26}\text{O}_{10}$, in the dried cotyledons, and *Barringtonia Vriesii* 1 per cent. in the bark, and 8 per cent. in the seeds, of the saponin $\text{C}_{18}\text{H}_{28}\text{O}_{10}$.

These saponins are closely related to others already obtained from other plants, and are readily hydrolysed in dilute solution by 2 per cent. sulphuric acid to saponin and sugar.

K. J. P. O.

Tannin contained in Sequoia Gigantea. By GEORG HEYL (*Chem. Centr.*, 1901, ii, 312—313; from *Pharm. Centr.-H.*, 42, 379—390).—The tannin, $\text{C}_{21}\text{H}_{20}\text{O}_{10}$, contained in the fir cones of *Sequoia gigantea*, is a pale reddish-brown powder, and is soluble in water, forming a solution which soon becomes turbid; it is soluble also in alkalis, ammonia, and alkali carbonates, forming reddish-brown solutions, and its alcoholic solution has a blood-red colour. It is insoluble in ether, chloroform, light petroleum, glacial acetic acid, or benzene, and gives a brownish-black precipitate with ferric chloride.

The bromo-derivative, $\text{C}_{21}\text{H}_{15}\text{O}_{10}\text{Br}_5$, the acetyl derivative, $\text{C}_{21}\text{H}_{14}\text{O}_{10}\text{Ac}_6$, and the benzoyl derivative, $\text{C}_{21}\text{H}_{14}\text{O}_{10}\text{Bz}_6$, are described. With salts of calcium, magnesium, barium, copper, or lead, the tannin gives precipitates which, when heated at 200°, yield pyrogallol, and when boiled with dilute sulphuric acid form mainly phlobaphene, together with some gallic acid and sugar. The tannin form, $\text{CH}_2(\text{C}_{21}\text{H}_{16}\text{O}_{10})_2$, is precipitated by formaldehyde from concentrated solutions of the tannin as a gela-

tinous mass, but separates from dilute solutions on adding hydrochloric acid in flesh coloured flakes ; it is insoluble in almost all solvents.

E. W. W.

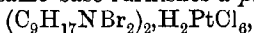
Pyromucic and isoPyromucic Acids. By CHAVANNE (*Compt. rend.*, 1901, 133, 167—169).—Pure *isopyromucic* acid melts at 91° ; 100 grams of water dissolve 4.5 grams of it, and only 2.7 grams of pyromucic acid at 0° . It dissolves unchanged in concentrated acids, but is decomposed by dilute alkalis. The *sodium* salt forms brilliant spangles, and gives an alkaline solution in water, which rapidly decomposes; the *potassium* salt is similar but extremely deliquescent; the *ammonium* salt loses ammonia in a vacuum. The *barium* salt, with $5\text{H}_2\text{O}$, and the *calcium* salt, with $3\text{H}_2\text{O}$, are sparingly soluble, crystalline powders; the *lead* salt contains $1\text{H}_2\text{O}$, and the *magnesium, zinc, cadmium, manganese, mercurous, and mercuric* salts are described. On mixing solutions of an alkali-salt of the acid and of copper sulphate, a red, crystalline, *cuprous* salt is formed; pyromucic acid, under similar conditions, gives the *cupric* salt with $3\text{H}_2\text{O}$.

isoPyromucic acid is not esterified by alcohol and dry hydrogen chloride, although pyromucic acid readily yields its ethyl ester under these conditions. Its oxidation by bromine water and by potassium permanganate is similar to that of pyromucic acid; but in addition, it reduces Fehling's solution in the cold, and acid or alkaline solutions of silver; with phenylhydrazine, it yields a compound, $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_2$, which crystallises in white needles, melts at 77° , gives the green coloration with ferric chloride characteristic of the parent acid, and is probably a *hydrazone* rather than a *hydrazide*, since its molecule requires for neutralisation the same quantity of alkali as the original acid. The phenylhydrazine derivative of pyromucic acid melts at 117° .

W. A. D.

Synthesis of Tropilidene. By RICHARD WILLSTÄTTER (*Annalen*, 1901, 317, 204—265. Compare this vol., i, 223).—The greater portion of the work discussed in this communication has already been published; the following data, however, are described for the first time.

The hydrogen chloride additive product of Δ^2 -methyltropan yields an *aurichloride*, $\text{C}_9\text{H}_{17}\text{N}\cdot\text{HAuCl}_4$, melting at $94\text{--}96^{\circ}$. The oily, basic dibromide of the same base furnishes a *platinichloride*,



crystallising in yellow needles and melting at $174\text{--}175^{\circ}$, and an *aurichloride* melting at $175\text{--}176^{\circ}$.

Ethyl Δ^2 -cycloheptenecarboxylate, $\text{C}_7\text{H}_{11}\cdot\text{CO}_2\text{Et}$, obtained by esterifying the acid with sulphuric acid and absolute alcohol, is a colourless oil having a fruity odour and boiling at 100° under 17 mm. pressure; it has a sp. gr. 0.9929 at $15^{\circ}/4^{\circ}$. This ester is hydrolysed only with great difficulty, and when it is decomposed by a hot solution of potassium hydroxide in methyl alcohol, the original acid is not regenerated, but the Δ^1 -isomeride is produced.

The *chloride*, $\text{C}_7\text{H}_{11}\cdot\text{COCl}$, of Δ^2 -cycloheptenecarboxylic acid is an oil boiling at $88\text{--}90^{\circ}$ under 13 mm. pressure. The corresponding *hydrazide*, $\text{C}_7\text{H}_{11}\cdot\text{CON}_2\text{H}_3$, produced by heating the ethyl ester with hydrazine hydrate at 120° , crystallises from water or ethyl acetate in

lustrous prisms melting at 137—139°, the *azide*, obtained from the hydrazide by the action of nitrous acid, is a colourless, explosive oil.

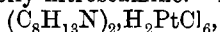
Tropilen, when reduced with zinc dust and acetic acid, yields a *ketone*, $C_7H_{12}O$, boiling at 169—170° (corr.); this substance, which gives a *semicarbazone* melting at 185—186°, is stable towards permanganate solution, and resembles the methylcyclohexanones.

The physical constants of the synthetical $\Delta^{1:3:5}$ -cycloheptatriene, $\begin{matrix} CH_2:CH:CH \\ CH_2:CH:CH \end{matrix} > CH$, are tabulated and compared with those of other hydrocarbons having seven-membered rings.

G. T. M.

Synthesis of Monocyclic Tropine Bases. By RICHARD WILLSTÄTTER (*Annalen*, 1901, 267—307. Compare this vol., i, 225 and preceding abstract).—The greater portion of the experimental part of this communication has already been published. The following compounds, however, are described for the first time.

Methylaminocycloheptadiene, $C_7H_9 \cdot NHMe$, obtained by treating tropilidene monohydrobromide with a benzene solution of methylamine, boils at 65—66° under 11 mm. and at 82° under 21.5 mm. pressure, it is somewhat soluble in cold water, but separates out when the solution is warmed. It readily absorbs carbon dioxide, forming a syrupy carbamate and yields an oily nitrosoamine. The *platinichloride*,



crystallises from water in orange-red prisms and melts at 154—155°; the *aurichloride*, when first precipitated, is oily, but rapidly solidifies to form orange-yellow needles melting at 85°. The *benzoyl* compound, $C_7H_9 \cdot NMeBz$, crystallises from light petroleum in rectangular plates and melts at 65—67°. The *phenylthiocarbamide*, $C_8H_{12}N \cdot CS \cdot C_6H_5N$, prepared by mixing its generators in ethereal solution, crystallises from alcohol either in white prisms, needles, or leaflets melting at 117—118°, or in colourless, four-sided plates melting at 125—126°. These forms, when crystallised separately, again yield crops containing both modifications. The remainder of the paper consists of a description of the preparation and properties of the Δ^2 , Δ^3 - and Δ^4 -methyltropans (dimethylaminocycloheptenes) and their salts, the results being exhibited in tabular form.

G. T. M.

Synthesis of Tropan and Tropidine. By RICHARD WILLSTÄTTER (*Annalen*, 1901, 317, 307—374. Compare this vol., i, 225, and preceding abstract).—The outline of these syntheses has been given in a previous communication.

The *platinichloride*, $(C_9H_{18}NCl)_2 \cdot H_2PtCl_6$, obtained from the additive product of Δ^4 -methyltropan and hydrogen chloride, crystallises from water either in prisms or four-sided plates and melts at 168°.

Tropan methiodide, $C_7H_{12}NMe_2I$, formed by treating the corresponding chloride with a concentrated solution of potassium iodide, crystallises from water in hopper-shaped aggregates and does not melt below 300°. Tropan methochloride, when heated above 300°, decomposes into tropan and methyl chloride.

The *platinichloride*, $(C_9H_{18}NCl)_2 \cdot H_2PtCl_6$, prepared from the additive product of Δ^3 -methyltropan and hydrogen chloride, crystallises from

water either in hexagonal plates or in sphenoidal forms, and melts at 178° ; the *aurichloride*, when crystallised in long needles, melts at $65-66^{\circ}$, but the melting point of different preparations is somewhat variable and indicates the existence of *cis*- and *trans*-modifications. The oily hydrogen chloride additive product itself is a mixture, for when dissolved in ether a portion undergoes rearrangement, yielding tropan methochloride, whilst the unchanged oil is stable even at 100° , furnishes a *platinichloride* melting at 183° , and is probably a derivative of the stable *cis-trans*-base.

Merling's partial synthesis of tropidine from α -methyltropidine leads to the production of a mixture of isotropidine and tropidine derivatives, in which the former predominate; the pure base has, however, been obtained from Δ^4 -methyltropan.

2-Bromotropan methiodide, formed by treating the corresponding methobromide with a concentrated solution of potassium iodide, crystallises in prisms; it melts and decomposes at 262° .

Δ^3 -Methyltropan forms a *dibromide* which changes into 6-bromotropan methobromide, a substance crystallising in acicular prisms and melting above 300° . The *platinichloride* of 6-bromotropan methochloride crystallises in hexagonal plates and melts at 250° . This bromotropan methobromide, when treated with alkalis, loses hydrogen bromide, yielding an unsaturated methobromide, which, when converted into the corresponding methochloride, furnishes a *platinichloride*,

$(C_8H_{13}NMe)_2PtCl_6$, crystallising in orange, acicular prisms melting at $233-234^{\circ}$, and an *aurichloride* forming yellow needles or leaflets melting at 258° .

isoTropidine methiodide, $CH \begin{array}{c} \swarrow CH_2 \cdot CH_2 \cdot CH_2 \\ \text{---} NMe_2 I \text{---} \\ \searrow CH = CH \end{array} CH$, produced by mix-

ing cycloheptadiene dibromide with a concentrated solution of methylamine in methyl alcohol or benzene and treating the tertiary base with methyl iodide, crystallises in four-sided plates and melts at 293° . From it, the methochloride is obtained which yields a *platinichloride*, $(C_9H_{13}NMe)_2PtCl_6$, crystallising in monoclinic prisms melting at $234-235^{\circ}$; and an *aurichloride* forming acicular prisms melting at $255-257^{\circ}$.
G. T. M.

Action of Pyridine Bases on Tetrahalogenated Benzoquinones. By HENRI IMBERT (*Compt. rend.*, 1901, 133, 162-164).—Pyridine combines with chloroanil in boiling ethyl acetate solution containing a small quantity of acetic acid to form a red compound, $OH \cdot C_5NH_2 : C_6Cl_2O_2$ or $C_5NH_4 \cdot C_6Cl_2O_2 \cdot OH$, which is soluble in dilute alkalis, except ammonia, and also in acids; boiling alkalis remove chlorine, but boiling hydrochloric acid merely dissolves the compound. Neither quinoline nor 2-methylpyridine combines with chloroanil either in ethyl acetate or acetic acid solution, but 3-methylpyridine yields a compound, $C_5NH_3Me \cdot C_6Cl_2O_2 \cdot OH$ or $OH \cdot C_5NHMe : C_6Cl_2O_2$, which forms a brownish-red mass of microscopic needles.

Bromoanil yields with pyridine a compound similar to that obtained from chloroanil.
W. A. D.

Action of Pyridine Bases on Tetrahalogen Derivatives of Quinone. By HENRI IMBERT (*Compt. rend.*, 1901, 133, 233—236. Compare preceding abstract).—When the pyridyldichlorohydroxyquinone formed by the action of pyridine on tetrachloroquinone is boiled with alcoholic or aqueous potash it yields a compound, $\text{OH}\cdot\text{C}_5\text{NH}_2\cdot\text{C}_6\text{ClO}_2\cdot\text{OK}$, or, more probably $\text{C}_5\text{NH}_4\cdot\text{C}_6\text{ClO}_2(\text{OK})\cdot\text{OH}$, the compound $\text{C}_5\text{NH}_4\cdot\text{C}_6\text{Cl}_2\text{O}_2\cdot\text{OK}$ being formed as an intermediate product. The final product forms orange-red crystals soluble in water, and when treated with sulphuric acid yields *pyridylchlorodihydroxyquinone*, $\text{C}_5\text{NH}_4\cdot\text{C}_6\text{ClO}_2(\text{OH})_2$, which crystallises in orange-red, microscopic needles soluble in hot alcohol, and in acids. It differs from pyridyldichlorohydroxyquinone in being generally more soluble, and producing a wine-red solution with alkalis. It is readily reduced by zinc and sulphuric acid, but not by sulphurous acid. The sodium salt is very soluble; the silver salt is brown and insoluble, and from it the *ethyl* and *benzoyl* salts can be obtained. They are both red, crystalline compounds. C. H. B.

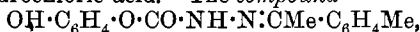
Carbazole. By WILHELM VAUBEL (*Zeit. angew. Chem.*, 1901, 14, 784—785).—A solution of carbazole in glacial acetic acid, when treated with nascent bromine from hydrochloric acid, and potassium bromide and bromate, decolorises 2 mols. of bromine but forms a monobromide (m. p. 197·5°), which is probably identical with the 3-bromocarbazole obtained by Ciamician and Silber (*Abstr.*, 1882, 1104). By the continued action of bromine, an impure *dibromide* melting at 170·5° was obtained. Carbazole may be titrated with bromine in glacial acetic acid solution, 2 mols. of bromine corresponding with 1 mol. of carbazole. R. H. P.

[Condensation Products of] **Formaldehyde.** By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1901, 25, 564).—Pentamethylenediamine condenses with a 40 per cent. solution of formaldehyde, precipitating a white compound, which is soluble in acids, but insoluble in alkalis, and decomposes when kept. A similar unstable, yellow *base* is obtained from *p*-phenylenediamine. *p*-Aminoacetanilide and formaldehyde condense in the presence of hydrochloric acid forming the *base*, $(\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2)_2\text{O}$, which is obtained as a white, crystalline powder. The analogous compound from *p*-aminophenol is an unstable, reddish, amorphous powder. R. H. P.

Carbohydrazides of the Dihydroxybenzenes. By ALFRED EINHORN and RICHARD ESCALES (*Annalen*, 1901, 317, 190—203. Compare *Abstr.*, 1898, i, 409).—Ketones of the type $\text{X}\cdot\text{COMe}$, where X is an aromatic radicle, condense with the carbohydrazides of the dihydroxybenzenes, yielding condensation products of the type $\text{OH}\cdot\text{C}_6\text{H}_3\cdot\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMeX}$, but, under similar conditions, this reaction does not take place with ketones such as acetone, diethyl ketone, ethyl acetoacetate, phenyl ethyl ketone, benzophenone, and the saturated cyclic ketones.

Acetophenone catecholcarbohydrazone, $\text{OH}\cdot\text{C}_6\text{H}_3\cdot\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMePh}$, produced, together with dicathecylcarbohydrazide,
 $\text{N}_2\text{H}_2(\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$,

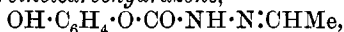
and *bisphenylmethy lazimethylene* (Curtius and Than, Abstr., 1891, 1355) by condensing catecholcarbohydrazide and acetophenone in the presence of glacial acetic acid or zinc chloride, crystallises from alcohol in nacreous leaflets and melts at 190—191°; it is soluble in solutions of the caustic alkalis, and is resolved into its generators on boiling with concentrated hydrochloric acid. The compound



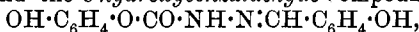
obtained from catecholcarbohydrazide and *p*-tolyl methyl ketone, crystallises in silky leaflets and melts at 185—186°.

Resorcinolcarbohydrazide, prepared by adding dry, powdered resorcinol carbonate to a cold solution of hydrazine hydrate in absolute alcohol and completing the action on the water-bath, crystallises from this solvent in white needles and melts at 160°.

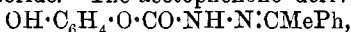
Acetaldehyde resorcinolcarbohydrazone,



obtained by treating the preceding compound with acetaldehyde, crystallises from water and melts at 150°; it is readily soluble in alcohol or acetone. The *benzaldehyde* compound, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CHPh}$, melts at 175°, and the *o*-hydroxybenzaldehyde compound,

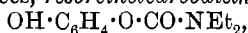


at 185—186°; the latter substance develops a greenish-black coloration with ferric chloride. The acetophenone derivative,



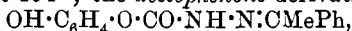
produced by mixing its generators in warm, alcoholic solution in the presence of glacial acetic acid, melts at 174°. The compound $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CMe}\cdot\text{C}_6\text{H}_4\text{Me}$, derived from resorcinolcarbohydrazide and *p*-tolyl methyl ketone, melts at 182°.

Resorcinol carbonate, when treated with diethylamine, yields a mixture of two substances, *resorcinolcarbodiethylamide*,



melting at 68—69°, and *resorcinoldicarbodiethylamide*, $\text{C}_6\text{H}_4(\text{O}\cdot\text{CO}\cdot\text{NEt})_2$, boiling at 270° under 36.5 mm. pressure and melting at 35—36°; these compounds are separated by the action of sodium hydroxide, in which the former alone is soluble.

Acetaldehyde quinolcarbohydrazone, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CHMe}$, produced from acetaldehyde and quinolcarbohydrazide, separates from water in white crusts and melts at 177°. The corresponding *benzaldehyde* compound crystallises in nacreous leaflets and melts at 215°; the *o*-hydroxybenzaldehyde compound is obtained in needles softening at 180° and melting at 194°; the *acetophenone* derivative,



forms needles melting at 120—121°, and its *p*-tolyl homologue melts at 208—209°.

G. T. M.

[Pyrazolone Derivatives from] Methyl α -Butyrylacetacetate. By A. BONGERT (*Compt. rend.*, 1901, 133, 165—167).—Whereas hydrazine acetate converts methyl α -butyrylacetacetate (this vol., i, 311 and 500) into methyl 5-methyl 3-propylpyrazole-4-carboxylate, hydrazine hydrate gives rise initially to acetylhydrazide and methyl butyrylacetate, the latter then condensing with a second mol. of hydrazine to

form 3-propyl-5-pyrazolone, which separates in white crystals and melts and sublimes at 196°.

The sodium derivative of methyl α -butyrylacetoacetate forms white crystals, melts at 142°, is not decomposed by cold water, and does not interact with methyl iodide. On adding methyl iodide, however, to a mixture of methyl α -butyrylacetoacetate and sodium methoxide, methyl acetate and methyl methylbutyrylacetate, $\text{COPr}_\alpha \cdot \text{CHMe} \cdot \text{CO}_2\text{Me}$, are formed. The latter boils at 86° under 16 mm. pressure. It combines with phenylhydrazine to form 1-phenyl-4-methyl-3-propyl-5-pyrazolone, which boils at 200° under 14 mm. pressure and separates from ether in white crystals melting at 78°. Hydrazine hydrate converts it into 4-methyl-3-propyl-5-pyrazolone, which forms white needles and melts at 189°.

Cold concentrated sulphuric acid hydrolyses methyl α -butyrylacetoacetate to butyric acid and methyl acetoacetate. W. A. D.

Nitroquinolones and Nitrocarbostyrils. By HERMAN DECKER (*J. pr. Chem.*, 1901, [ii], 64, 85—101).—In the literature, seven nitrocarbostyrils are described in which the nitro-group is in the benzene nucleus, whilst only four such compounds are theoretically possible. The author has reinvestigated these compounds, and studied the nitration of the 1-alkyl-2-quinolones and nitro-1-alkyl-2-quinolones.

6-Nitro-1-methyl-2-quinolone, $\text{C}_{10}\text{H}_8\text{O}_3\text{N}_2$, prepared by oxidising 6-nitroquinoline methiodide, crystallises in pale yellow needles melting at 222°. The corresponding *ethyl* derivative forms pale yellow needles melting at 183°.

7-Nitro-1-methyl-2-quinolone, prepared by oxidising 7-nitroquinoline methiodide or methyl sulphate, crystallises in yellow needles melting at 198—199°. 7-Nitroquinoline ethiodide forms large, ruby-red needles; 7-nitro-1-ethyl-2-quinolone, lustrous needles melting at 168—169°.

[With N. KASATKIN].—The so-called [γ] nitrocarbostyryl (Friedländer and Lazarus, *Abstr.*, 1885, 1138) is 6-nitrocarbostyryl (6-nitro-2-hydroxyquinoline), as the sodium derivative yields 6-nitro-1-methyl-2-quinolone (m. p. 222°) with methyl iodide. The nitrobromocarbostyryl (*Abstr.*, 1892, 630) is then 3-bromo-6-nitro-2-hydroxyquinoline.

[With G. POLLITZ].—[ϵ] Nitrocarbostyryl (m. p. 302°) yields on alkylation 5-nitro-1-methyl-2-quinolone (m. p. 135°) and 5-nitro-1-ethyl-2-quinolone (m. p. 166°) respectively, and is therefore 5-nitrocarbostyryl (compare Claus and Setzer, *Abstr.*, 1896, i, 498). [ϵ] Nitro-2-bromoquinoline, from which the nitrocarbostyryl is obtained by the action of concentrated hydrochloric acid, has also the nitro-group in position 5.

[δ] Nitrocarbostyryl (m. p. 163°; Miller and Kinkelin, *Abstr.*, 1889, 990), which is prepared in a similar manner from [δ] nitro-2-bromoquinoline, is 8-nitrocarbostyryl, as it yields on alkylation, nitro-alkyl-2-quinolones isomeric with the preceding. 8-Nitro-1-methyl-2-quinolone, prepared by boiling [δ] nitrocarbostyryl with methyl sulphate and concentrated sodium hydroxide, crystallises in long needles melting at 124—125°; the corresponding *ethyl* derivative forms needles or plates melting at 92°. 2-Bromoquinoline, on

nitration, yields therefore in the normal manner 5- and 8-nitro-2-bromoquinolines.

[ζ] Nitro-2-bromoquinoline (m. p. 244° ; Claus and Pollitz, Abstr., 1890, 521) is not homogeneous, as it yields a mixture of 5- and 8-nitro-1-methyl-2-quinolones. [ζ] Nitrocarbostyryl (m. p. 283°) is therefore a mixture of 5- and 8-nitrocarbostyryl.

Quinoline methyl sulphate yields on nitration only 5-nitromethylquinoline (compare Abstr., 1900, i, 689).

1-Methyl-2-quinolone yields on nitration with nitric acid (sp. gr. 1.4) only the 5-nitro-derivative, but with fuming nitric acid a mixture of mono-, di-, and tri-nitro-derivatives. *Trinitro-1-methyl-2-quinolone*, $C_9NH_3OMe(NO_2)_3$, crystallises in lustrous, pale yellow, insoluble needles, melting at $208-210^{\circ}$. 1-Ethyl-2-quinolone behaves in a similar manner. *Trinitro-1-ethyl-2-quinolone* forms dark yellow crystals melting at 224° . The nitration of the 1-alkylquinolones and of carbostyryl is far more easily effected than that of quinoline.

Trinitro-1-methyl-2-quinolone, $C_9NH_3OMe(NO_2)_3$, prepared by nitration of 7-nitro-1-methyl-2-quinolone, forms large, orange-yellow crystals melting and decomposing at 249° . *Trinitro-1-ethyl-2-quinolone*, prepared similarly from 7-nitro-1-ethyl-2-quinolone, forms plates melting and decomposing at 237° .

7-Nitrocarbostyryl is prepared from 7-nitroquinoline, which is treated with hypochlorous acid, and the additive product decomposed by sodium hydroxide; it crystallises in lustrous, pale-yellow, insoluble needles, melting at 340° .

Of [α] and [β] nitrocarbostyryl (Friedländer and Lazarus, *loc. cit.*), the author believes that the former is identical with 7-nitrocarbostyryl, whilst the latter is either very impure 6-nitrocarbostyryl or the nitro-group is in the pyridine nucleus.

K. J. P. O.

Hydrochloride of Phenylhydrazine Ureide [Diphenylcarbazine]. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1901, [iii], 25, 757-758. Compare this vol., i, 292).—*Diphenylcarbazine hydrochloride*, $C_{13}H_{14}ON_4.HCl$, is prepared by adding a large excess of a saturated ethereal solution of hydrogen chloride to an alcoholic solution of diphenylcarbazine; it forms cauliflower-like masses of small white crystals, melting and decomposing at 125° .

N. L.

Violet Chromium Colouring Matters derived from Diphenylcarbazine. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1901, [iii], 25, 758-761).—The violet colouring matter (Abstr., 1900, ii, 627) formed by the action of diphenylcarbazine on chromic acid has been obtained in the form of a violet-black, amorphous powder, the composition of which varies with the conditions of its preparation; its tinctorial properties are of no practical interest. A similar compound is formed by dimethyldiphenylcarbazine, but not by diphenylcarbazine. N. L.

α -Azoxynaphthalene. By LEONHARD WACKER (*Annalen*, 1901, 317, 375-385).—The amorphous compound obtained by Jaworsky (*J. pr. Chem.*, 1865, 94, 283) on reducing α -nitronaphthalene with sodium amalgam in alcoholic solution is also produced by reducing the nitro-compound with zinc dust and alcoholic potassium hydroxide

solution. It does not seem to have the properties of an azoxy-compound, and does not yield α -azonaphthalene on reduction.

A crystalline α -azoxynaphthalene is prepared together with α -naphthylhydroxylamine, by reducing α -nitronaphthalene with zinc dust in dilute alcoholic solution containing ammonium chloride; it is also formed, together with α -naphthylamine, when α -naphthylhydroxylamine is heated on the water-bath.

It slowly separates from acetone or light petroleum in thick, red prisms, and from alcohol in yellow, or reddish-brown, rhombic crystals; the former modification melts at 126.5° and the latter at 127° , both forms have the same chemical properties, and belong to the rhombic system. A solution of the substance in concentrated sulphuric acid is reddish-violet, slowly changing into blue; when warmed with more dilute acid (65 per cent. H_2SO_4), the α -azoxynaphthalene dissolves, yielding a blue solution, from which water precipitates a compound, soluble in aqueous sodium hydroxide to a red solution. These changes indicate a transformation of the azoxy-compound into a hydroxyazo-derivative. Filter paper soaked in the dilute, yellow, alcoholic solution of the azoxy-compound, soon becomes red when exposed to sunlight; a similar phenomenon is noticed in the case of azoxybenzene. α -Azonaphthalene is produced by the reduction of the new azoxy-derivative with zinc dust in an alcoholic solution of potassium hydroxide.

G. T. M.

Decomposition Products of Edestin. By P. A. LEVENE and LAFAYETTE B. MENDEL (*Amer. J. Physiol.*, 1901, 6, 48—52).—The crystallised vegetable proteid edestin resembles the ordinary animal proteids in yielding the three known hexon bases, and so differs from the vegetable proteids, which are soluble in alcohol, and yield no lysine.

W. D. H.

Action of Reducing Agents on Hæmatin. By J. A. MILROY (*Proc. Physiol. Soc.*, 1901, xiv—xvi).—Hæmin was prepared by crystallisation from acetone containing hydrochloric acid: hæmatin was prepared from this, dissolved in glacial acetic acid and reduced by aluminium powder. After 24 hours, a bright red reduction product is formed which gives spectroscopic bands similar to those of oxyhæmoglobin, with the addition of a faint band in the red. This substance is soluble in chloroform and in ammonia; in ammonia, it shows no change in the absorption bands. It contains only a trace of iron, possibly due to the adherence of some unchanged hæmatin. After re-solution in glacial acetic acid and further reduction with zinc dust between 50° and 60° , the solution becomes green, and shows two absorption bands, one on each side of the D line; in this, it resembles the bilicyanin of Heynsius and Campbell. In chloroform, it becomes greenish-blue with a red fluorescence. It is soluble in dilute alkalis, but readily undergoes changes on exposure to air. The examination of these substances is not yet completed.

W. D. H.

Organic Chemistry.

Trimethyltrimethylenes. By NICOLAI D. ZELINSKY and J. ZELIKOFF (*Ber.*, 1901, 34, 2856—2867).—When diacetonealcohol is reduced with sodium amalgam, it forms *trimethyltrimethylene glycol*, $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH}$, which is a sweet, viscous liquid boiling at $135\text{--}136^\circ$ under 40 mm. pressure, has a sp. gr. 0.9254 at $17^\circ/4^\circ$, and a refraction $n = 1.4311$ at 17° , and when treated with hydrogen bromide yields the *dibromide*, $\text{CMe}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CHMeBr}$, which boils at 82° under 21 mm. pressure and has a sp. gr. 1.5316 at $20^\circ/4^\circ$.

1:1:2-Trimethyltrimethylene, $\text{CMe}_2 \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CHMe} \end{smallmatrix}$, obtained by reducing the dibromide with zinc dust, boils at $56\text{--}57^\circ$ under 750 mm. pressure, has a sp. gr. 0.6822 at $19.5^\circ/4^\circ$, a refraction $n_D = 1.3848$ at 19.5° , decolorises permanganate very slowly, and is distinct from the hexylene described by Couturier (*Abstr.*, 1893, i, 245), whose work has been repeated and confirmed by the present authors.

Methylacetylacetone, when reduced with sodium amalgam, yields a mixture of the *ketonealcohol*, $\text{CHMeAc} \cdot \text{CHMe} \cdot \text{OH}$, which boils at $104\text{--}107^\circ$ under 20 mm. pressure, has a sp. gr. 0.9937 at $18^\circ/4^\circ$, and a refraction $n_D = 1.4512$ at 18° , and the *trimethyltrimethylene glycol*, $\text{OH} \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{OH}$, which boils at $113\text{--}116^\circ$ under 20 mm. pressure, has a sp. gr. 0.9906 at $14^\circ/4^\circ$, and a refraction $n_D = 1.4524$ at 14° . The glycol, when treated with hydrogen bromide, forms a *dibromide* which boils at $95\text{--}100^\circ$ under 30 mm. pressure, and when reduced with zinc dust yields 1:2:3-trimethyltrimethylene.

1:2:3-Trimethyltrimethylene, $\text{CMe} \begin{smallmatrix} \text{CMe} \\ | \\ \text{CMe} \end{smallmatrix}$, boils at $65\text{--}66^\circ$ under 748 mm. pressure, has a sp. gr. 0.6921 at $22^\circ/4^\circ$, and a refraction $n_D = 1.3942$ at 22° . The *diiodide* corresponding with the dibromide, when reduced with zinc dust, yields the γ -methylpentane described by Wislicenus (*Abstr.*, 1883, 967), whose work has been repeated and confirmed by the present authors.

R. H. P.

The so-called Iodoacetylene. By ALBERTO PERATONER and R. SPALLINO (*Ber.*, 1901, 34, 2718—2722).—The non-poisonous iodoacetylene described by Paternò and Peratoner (*Abstr.*, 1890, 1219) can only be obtained from the impure acetylene prepared by the action of hydrochloric acid on copper acetylide, and is shown to be a mixture of solid diiodoacetylene, acetylene, vinyl chloride, and ethylidene dichloride. The only known iodo-derivative of acetylene is therefore the poisonous and malodorous compound prepared by Baeyer (*Abstr.*, 1885, 1199) and shown by Nef (*Abstr.*, 1889, i, 104) to be a diiodoacetylene.

T. M. L.

The Rendering Active of Oxygen. VII. By CARL ENGLER and WILHELM FRANKENSTEIN (*Ber.*, 1901, 34, 2933—2941. Compare *Abstr.*, 1897, ii, 402; 1899, i, 189, 221; 1900, i, 399).—A consider-

able precipitate of a *diperoxide*, $C_8H_{10}O_4$, is produced when a 5—7 per cent. benzene solution of dimethylfulvene [*isopropylidenecyclopentene*] (Thiele, Abstr., 1900, i, 299) is stirred automatically in contact with the air or is shaken automatically in a bottle the air in which is repeatedly renewed. The oxidation is complete after 4—6 days. The same product is formed, only more slowly, when air or oxygen is passed through the solution without stirring. Light and a rise in temperature are two important factors which accelerate the precipitation; when, however, the temperature is too high, secondary reactions occur, and the original insoluble oxidation product becomes converted into substances soluble in benzene. Dimethylfulvene diperoxide forms a colourless powder, which explodes at 130° , and also when warmed with concentrated sulphuric acid. It is insoluble in most organic solvents, but dissolves in nitrobenzene, acetic acid, or alkalis, but at the same time is decomposed. It does not give the usual test for peroxides, namely, a yellow coloration with titanous acid, unless ether, alcohol, ethyl acetate, or chloroform is present.

Methylethylfulvene [β -*butylidenecyclopentene*] is an orange-coloured liquid boiling at 185° under atmospheric pressure, and also yields a peroxide. Methylphenylfulvene also absorbs oxygen, but less readily than the simple alkyl fulvenes; the *diperoxide*, $C_{13}H_{12}O_4$, can be precipitated from the benzene solution by the aid of ether, but when once precipitated will not dissolve in benzene.

*cyclo*Pentadiene also absorbs oxygen, but so far no definite product has been isolated. The oxidation of hexylene and of dimethylfulvene has been studied by the aid of *N*/25 sodium indigotindisulphonate as described in the case of pentane. The numbers in the case of hexylene point to the direct addition of 1 mol. of oxygen, and the subsequent transference of one atom to the indigo. J. J. S.

Basic Properties of Oxygen. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1901, 34, 2679—2698).—All classes of organic oxygen compounds form salt-like derivatives with complex acids, whilst in a few cases similar compounds are formed with simple acids, the salts of dimethylpyrone, described by Collie and Tickle (*Trans.*, 1899, 75, 710), being of this class. Each basic oxygen atom is capable of combining with an amount of acid equivalent to one hydrogen ion, normal and acid salts being formed with polybasic acids. The constitution of these compounds cannot be expressed in terms of the ordinary formulæ, in which oxygen is bivalent, but may be expressed by supposing either that the oxygen in these compounds is quadrivalent (oxonium theory of Collie and Tickle), or that these salts are complex compounds (Werner), oxygen possessing one complex and two ordinary valencies. Which of the two theories is the more applicable to the facts has not yet been decided. The introduction of positive groups into an oxygen compound appears to increase the basicity, as it does in the case of ammonia, whilst negative groups diminish it, and it also appears to be the case that the less stable the form of combination of the oxygen, the greater the tendency to form salts. The following salts, representative of the various classes of organic oxygen compounds, have been prepared.

1. *Ethers*.—Ethyl ether, when added to an acid solution of potassium ferrocyanide, produces a crystalline precipitate of a *compound* of ethyl ether with ferrocyanic acid, which, however, rapidly decomposes and changes in appearance.

Ferricyanic and cobalticyanic acids behave in a similar manner. Diisoamyl ether combines with ferricyanic acid, and unites with cobalticyanic acid to form a *compound*, $C_{10}H_{22}O, H_3Co(CN)_6, 2H_2O$, which crystallises like ammonium chloride and is decomposed by water. Anisole with ferricyanic acid yields six-sided tablets, and phenetole gives a solid film; paraldehyde with ferrocyanic acid gives large, rhombic plates.

2. *Ethylene Oxide and allied Substances*.—Ethylene oxide forms a crystalline compound at a low temperature with ferrocyanic acid. Cineol forms crystalline salts with simple acids, the hydrochloride and hydrobromide having been already described by Wallach (*Annalen*, 1884, 225, 297; 1888, 246, 280). The *phosphate* is a gelatinous mass; the *hydroferrocyanide*, $2C_{10}H_{18}O, H_4Fe(CN)_6, \frac{1}{2}H_2O$, is a white powder; the *hydroferricyanide* has the composition $2C_{10}H_{18}O, H_3Fe(CN)_6, 3H_2O$, and unites with 1 mol. of acetone. The *hydrocobalticyanide* crystallises in colourless needles and may be used for the preparation of pure cobalticyanic acid. Pinol yields a crystalline *compound* with ferricyanic acid, and an amorphous one with ferrocyanic acid.

3. *Alcohols*.—The *compound* of amyl alcohol and ferricyanic acid crystallises in needles. Borneol unites with all three acids. The *hydrocobalticyanide* has the composition $2C_{10}H_{18}O, H_3Co(CN)_6$. Menthol and tetrahydrocarveol give with ferricyanic acid indistinctly crystalline powders. Trimethylcarbinol and amylene hydrate unite with ferrocyanic acid, whilst *isobutyl* alcohol does not.

4. *Acids*.—The only compound of this class appears to be the perbromide of the hydrobromide of acetic acid (Steiner, this Journ., 1874, 566).

5. *Esters*.—Ferricyanic acid unites with ethyl acetate, yielding flat prisms; with ethyl benzoate, forming orange-coloured needles; with ethyl oxalate, giving rhombic tablets; and with *isoamyl* valerate, yielding an indistinctly crystalline powder. With ferrocyanic acid, ethyl oxalate readily yields large, rhombic tablets of the formula $C_6H_{10}O_4, H_4Fe(CN)_6$.

6. *Aldehydes*.—Heptaldehyde does not unite with ferrocyanic acid, but forms a crystalline powder with ferricyanic acid. Benzaldehyde gives an amorphous compound with ferrocyanic acid, orange-coloured needles with ferricyanic acid, and thin prisms with cobalticyanic acid. Cinnamaldehyde has long been known to form a nitrate (Dumas and Peligot, *Annalen*, 1835, 14, 65). It also forms, with ferrocyanic acid, rhombic tablets, with ferricyanic acid a crystalline powder, and with chloroplatinic acid orange-red prisms of the *platinichloride*.

7. *Ketones*.—Diethyl ketone yields rhombic plates with ferrocyanic acid, and a crystalline powder with ferricyanic acid. Dipropyl ketone gives irregular plates with ferrocyanic acid, and an oil with ferricyanic acid. Acetophenone gives rhombic plates with ferrocyanic acid, and an amorphous compound with ferricyanic acid. 1:3-Methylcyclohexanone yields a crystalline powder with ferrocyanic acid and small needles with ferricyanic acid. Menthone forms an indistinctly crys-

talline powder with ferrocyanic acid and small needles with ferricyanic acid. Tetrahydrocarvone gives long needles with ferrocyanic acid and a crystalline powder with ferricyanic acid. Suberone yields small prisms with ferrocyanic acid, and small needles with ferricyanic acid. *p*-Diketohexamethylene unites with phosphotungstic acid to form a compound which crystallises from water in well-developed, long tablets. Several compounds of camphor with acids are already known. The *hydrocobalticyanide* is a crystalline powder of the formula $2C_{10}H_{16}O, H_3Co(CN)_6, 2H_2O$. Fenchone and carone also give compounds, both with ferrocyanic and ferricyanic acid. Mesityl oxide yields an amorphous compound with ferricyanic acid, and a crystalline powder with ferrocyanic acid; phorone yields a crystalline compound with ferrocyanic acid, benzylideneacetone forms an amorphous compound with ferricyanic acid, a powder consisting of small tablets with ferrocyanic acid, and a *platinichloride*, $2C_{10}H_{16}O, H_2PtCl_6, 2H_2O$, which crystallises in thin, orange-yellow prisms. Dibenzylideneacetone yields an orange-coloured, amorphous compound with ferricyanic acid, and a cinnabar-red, amorphous powder with phosphotungstic acid. The hydrochloride has previously been described by Claisen and Ponder (*Annalen*, 1884, 223, 142) as a red powder. In order to ascertain whether this compound was a salt or a chlorohydrin, the corresponding *dichloro*-derivative, $CHPh \cdot CH \cdot CCl_2 \cdot CH \cdot CHPh$, was prepared by the action of phosphorus pentachloride on the hydrochloride, and crystallises in colourless, lustrous plates melting at 78° . Since this compound is colourless, it follows that the hydrochloride cannot have a similar constitution. The dichloride itself is coloured yellow by hydrochloric acid, probably owing to the formation of an unstable salt. Carvenone yields an amorphous compound with ferrocyanic acid and small needles with ferricyanic acid. Inactive dihydrocarvone yields with ferrocyanic acid a crystalline powder and with ferricyanic acid an amorphous film. Quinone dissolves in syrupy phosphoric acid and is precipitated by water. With phosphotungstic acid, it forms a compound which crystallises in six-sided tablets. Similar salts of substances containing quinonoid oxygen, such as aurin and fluorescein, have long been known. Dimethylpyrone, in addition to the compounds described by Collie and Tickle, appears to form a *dihydrochloride* when the hydrochloride is exposed to hydrogen chloride. The hydrochloride reacts with potassium ferrocyanide and ferricyanide, crystalline salts of the complex acids being precipitated. The pyrone also unites with cobalticyanic acid to form rhombic tablets, and with phosphotungstic acid to form small needles.

Several cases of the combination of unsaturated compounds containing an ethylene linking with complex acids have also been observed, and it appears probable that these compounds are also capable of forming salts.

A. H.

Synthesis of Tertiary Cyclic Alcohols by the Aid of Magnesiumalkylhaloids. By NICOLAI D. ZELINSKY (*Ber.*, 1901, 34, 2877—2884. Compare Barbier, *Abstr.*, 1899, i, 323; Grignard, 1900, i, 382; this vol., i, 250, 263; Blaise, this vol., i, 317).—The following method is recommended for the preparation of tertiary cyclic alcohols.

An alkyl iodide (1 mol.) is carefully added to magnesium (1 atom.), covered with dry ether, and to this mixture an ethereal solution of the cyclic ketone (1 mol.) is gradually run in. Acidified water is added, and the ethereal solution separated, and dried with potassium carbonate.

1-Methylcyclohexanol-1, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CMe} \cdot \text{OH}$, obtained from cyclohexanone, is a colourless oil, distils at $156-158^\circ$, and has a sp. gr. 0.9194 at $26^\circ/4^\circ$, and n_D 1.4558 at 26° .

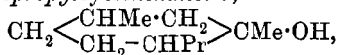
1:3-Dimethylcyclohexanol-3, from 1-methylcyclohexanone-3, distils at $67-68^\circ$ under 16 mm. pressure, has a sp. gr. 0.8983 at $23^\circ/4^\circ$, n_D 1.4523 at 23° , and is slightly dextrorotatory.

1-Methyl-3-ethylcyclohexanol-3 distils at $80-81^\circ$ under 16 mm. pressure, and has a sp. gr. 0.8995 at $26^\circ/4^\circ$, n_D 1.4545 at 26° , and $[\alpha]_D +1.48^\circ$.

1-Methyl-3-propylcyclohexanol-1 distils at $94-96^\circ$ under 18 mm., or at $198-200^\circ$ under atmospheric pressure, and has a sp. gr. 0.8903 at $24^\circ/4^\circ$, and n_D 1.4566 at 24° . The corresponding isopropyl derivative boils at $81-83^\circ$ under 14 mm., or at $186-188^\circ$ under atmospheric pressure, but is always accompanied by a considerable amount of a hydrocarbon distilling at $152-153^\circ$ under 14 mm. pressure.

A hydrocarbon, $\text{C}_{20}\text{H}_{38}$, boiling at 260° , is formed by the action of acetone on magnesium, dry ether, and 1-methylcyclohexyl-3 iodide and subsequent treatment of the product with acidified water.

1:3-Dimethyl-4-isopropylcyclohexanol-3,



obtained from menthone, boils at 100° under 20 mm. pressure, and has a sp. gr. 0.8952 at $25^\circ/4^\circ$ and $[\alpha]_D +12^\circ 22'$. *d*-Fenchone yields methylfenchyl alcohol, $\text{C}_{10}\text{H}_{16}\text{Me} \cdot \text{OH}$, distilling at $100-102^\circ$ under 22 mm., or at $208-209^\circ$ under atmospheric pressure; it melts at $51-52^\circ$, and has $[\alpha]_D +11^\circ$. Methylborneol, obtained from ordinary camphor, melts at $154-156^\circ$, readily sublimes, distils at about 193° , and has $[\alpha]_D 30^\circ 79'$ in alcoholic solution.

Dimethylcyclopropylcarbinol, $\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CMe}_2 \cdot \text{OH}$, from acetotri-methylene, distils at 123° under 740 mm. pressure, and has a sp. gr. 0.8791 at $24^\circ/4^\circ$, and n_D 1.4309 at 24° . J. J. S.

Esterification of Glycerol. By CARL BOETTINGER (*Chem. Zeit.*, 1901, 25, 795-797 and 811-812).—Pure glycerol has been mixed with known weights of the following acids: tartaric, succinic, malic, maleic, fumaric, citric, formic, acetic, chloroacetic, glycollic, and glyoxylic acids. Each mixture was left at the ordinary temperature for some time and then the amount of standard alkali required to neutralise the unesterified acid determined. Similar experiments were carried out (1) with the addition of one to two drops of hydrochloric acid, (2) at a higher temperature. The esterification was accelerated by both these methods. J. J. S.

Nitromannitol and Nitrocellulose. By LEO VIGNON and F. GERIN (*Compt. rend.*, 1901, 133, 515—517).—Pentanitromannitol and hexanitromannitol, obtained by the action of sulphuric and nitric acids on mannitol, readily reduce Fehling's solution, and thus resemble the nitrocelluloses (Abstr., 1900, i, 589, 628, 629); they have no action on Schiff's reagent, however, and in this respect differ from the nitrocelluloses. A further difference is found in the fact that whereas the nitrocelluloses give oxytcelluloses when treated with ferrous chloride, the nitromannitols yield mannitol, which has no reducing power. The cupric reducing power of nitromannitol is greater than that of dextrose, but is not due to the presence of mannose. C. H. B.

Preparation of Alkyl and Aryl Carbonates. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117624; Eng. Pat. 530 of 1900).—The additive compound, $\text{CO}(\text{C}_5\text{H}_7\text{ON}_2\text{PhCl})_2$, of antipyrine with carbonyl chloride reacts with alcohols and phenols, yielding the corresponding carbonates; methyl and *n*-propyl chlorocarbonates are produced by the use of methyl and *n*-propyl alcohols respectively. *Methyl-*n*-propylcarbinyl chlorocarbonate*, $\text{CHMePr}^{\alpha}\cdot\text{O}\cdot\text{COCl}$, an oil boiling at 68° under 26 mm., and at $140\text{--}145^\circ$ under atmospheric pressure, is obtained from methyl-*n*-propylcarbinol, whilst *menthyl chlorocarbonate* boiling at $105\text{--}106^\circ$ under 12 mm. pressure results from the interaction of antipyrine carbonyl chloride and menthol. *Guaiacol chlorocarbonate*, prepared in a similar manner, is a colourless oil boiling at 112° under 25 mm. pressure.

The compound $\text{OMe}\cdot\text{C}_5\text{NH}_5\cdot\text{CO}\cdot\text{C}_5\text{NH}_5\text{Cl}$, produced from methyl chlorocarbonate and pyridine in benzene solution, yields alkyl or aryl carbonates when treated with water, alcohols, or phenols. Dimethyl carbonate is obtained by the action of water, and methyl benzyl carbonate results from the action of benzyl alcohol on this additive compound.

The compound $\text{CO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Ph})_2$ is produced from salol and the additive compound of pyridine and salol chlorocarbonate, the compound $\text{OEt}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Ph}$ being obtained by the action of alcohol on the same pyridine derivative. G. T. M.

Alkyl Carbonates. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117625. Compare preceding abstract).—*Methyl-*n*-propylcarbinyl carbonate*, $\text{CO}(\text{O}\cdot\text{CHMePr}^{\alpha})_2$, a colourless oil having a slightly aromatic odour and boiling at $205\text{--}207^\circ$, results from the action of methyl-*n*-propylcarbinol on the additive compound of pyridine and carbonyl chloride. In a similar manner, the dimethyl and diethyl carbonates are obtained by the action of the corresponding alcohols on this pyridine derivative. G. T. M.

Carbamates of the Secondary Alcohols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 120863. Compare D.R.-P. 114396).—The *chlorocarbonates* of methylethyl-, diethyl-, methylpropyl-, methylisopropyl-, ethylpropyl-, ethylisopropyl-, methylbutyl-, and dipropyl-carbinols are liquids having an irritating odour and boil respectively at $121\text{--}122^\circ$, $131\text{--}133^\circ$, $140\text{--}141^\circ$, $130\text{--}132^\circ$, $141\text{--}143^\circ$, $144\text{--}146^\circ$, $144\text{--}146^\circ$,

and 157—159°. Methyl isopropyl-carbamate may be obtained either by heating methyl isopropylchloro-carbonate with ammonia in an indifferent solvent, or by slowly adding carbamide hydrochloride to methyl isopropylcarbinol; it melts at 86—87°. The corresponding methylbutyl compound crystallises in white needles and melts at 56°. These two methods are applicable to the preparation of the homologous alkyl carbamates. G. T. M.

Carbamates of the Secondary Alcohols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 120864. Compare preceding abstract).—The carbamates of the secondary alcohols may be obtained by treating the secondary alcohols with cyanogen chloride or cyanic acid dissolved in an indifferent solvent, and also by the action of ammonia on the corresponding dialkyl carbonates. The *dialkyl carbonates* obtained from methylethyl-, diethyl-, methylpropyl-, methylisopropyl-, ethylpropyl-, ethylisopropyl-, methylbutyl-, and dipropyl-carbinols are liquids boiling respectively at 178—180°, 205—207°, 208—210°, 205—207°, 233—234°, 227—228°, 239—240°, and 260—265°. G. T. M.

Carbamates of the Secondary Alcohols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 120865. Compare preceding abstracts).—*Methyl-n-butylcarbinyl carbamate*, $\text{NH}_2 \cdot \text{CO}_2 \cdot \text{CHMe} \cdot \text{CH}_2\text{Pr}$, the *urethane* of methyl-n-butylcarbinol, melts at 65—66°; its higher homologue, $\text{NH}_2 \cdot \text{CO}_2 \cdot \text{CHEt} \cdot \text{CH}_2\text{Pr}$, melts at 80—81°; these compounds are prepared either by the action of urea nitrate on the corresponding secondary alcohols, or by the reactions indicated in the preceding abstracts. The *chlorocarbonates*, prepared from ethylisobutyl-, methyl-n-butyl-, and methyl-n-pentyl-carbinols, boil respectively at 155—157°, 144—146°, and 154—156° under the ordinary pressure. The *dialkyl carbonates* obtained from ethylisobutyl-, methyl-n-butyl-, and methyl-n-pentyl-carbinols boil at 250—255°, 228—230°, and 249—250° respectively. G. T. M.

Composition of Cocoa Butter. Preliminary Communication. By J. KLIMONT (*Ber.*, 1901, **34**, 2636).—Cocoa butter may be separated by fractional crystallisation from acetone into three fractions: 1. A mixture of palmitin and stearin melting at 70°. 2. Palmitic-oleic-stearic triglyceride, $\text{C}_{55}\text{H}_{104}\text{O}_6$, which melts at 31—32°, crystallises in nodules, and has the iodine number 28.9 and the saponification number 196.4. 3. A mixed glyceride, $\text{C}_{51}\text{H}_{96}\text{O}_6$, which melts at 26—27°, and has the iodine number 31.7 and the saponification number 210.5. A. H.

Action of Fuming Nitric Acid on Substituted Acrylic Acids. By A. WAHL (*Bull. Soc. Chim.*, 1901, [iii], **25**, 804—808).—The action of fuming nitric acid on ethyl crotonate takes place with difficulty, and results in the formation of a small quantity of *ethyl nitrocrotonate*, a pale yellow liquid boiling at 100—106° under 13 mm. pressure. When ethyl tiglate is treated with fuming nitric acid, fixation of the latter occurs, but no well-defined product seems to be formed. Ethyl isolauronolate, when similarly treated, yields a *nitrate*, $\text{C}_{11}\text{H}_{19}\text{O}_5\text{N}$, which crystallises in colourless prisms melting at 79—80°, and regenerates the original ester on reduction with aluminium

amalgam. From methyl cinnamate, a mixture of methyl *o*- and *p*-nitrocinnamates is obtained. N. L.

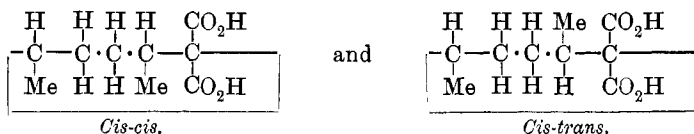
Constitution of α - and β -Nitrodimethylacrylic Esters. By LOUIS BOUVEAULT and A. WAHL (*Bull. Soc. Chim.*, 1901, [iii], 25, 808—817).—The experimental results described in this paper have been already noticed (this vol., i, 5). The question of the constitution of the potassium salt of ethyl β -nitrodimethylacrylate and analogous compounds is now discussed, the views of V. Meyer, Michael, Nef, and Hantzsch being referred to. N. L.

Camphoric Acid. X. Racemic Campholytic Acid and Racemic Dihydrohydroxycampholytic Acid. By WILLIAM A. NOYES and W. M. BLANCHARD (*Amer. Chem. J.*, 1901, 26, 281—292).—Racemic α -campholytic acid (Walker and Cormack, *Trans.*, 1900, 77, 380) boils at 127—128° under 14 mm. pressure, and forms crystals melting at 31°. When its hydrobromide is treated with sodium hydroxide, in addition to the regenerated acid, *racemic dihydrohydroxycampholytic acid* is produced, which crystallises in needles from ethyl acetate or water, and if warmed with dilute sulphuric acid is converted into β -campholytic acid. This acid can be resolved into its optically active components by fractional crystallisation of the strychnine salts; the *d*-acid thus obtained is identical with that prepared from aminodihydrocampholytic acid (*Abstr.*, 1895, i, 295). By the action of bromine on racemic α -campholytic acid, dibromo- α -campholytic acid melting at 109° and dibromo- β -campholytic acid melting at 141° are produced.

Racemic dihydro- α -campholytic acid, $C_8H_{15} \cdot CO_2H$, obtained by reducing the hydriodide of *i*- α -campholytic acid with zinc dust, boils at 245—247°; its *amide* crystallises in needles and melts at 103—104°. *α -Bromodihydro- i - α -campholytic acid*, $C_8H_{14}Br \cdot CO_2H$, obtained by treating the acid with phosphorus pentachloride and warming the resulting chloride with bromine in a sealed tube, crystallises in needles and melts at 148°. By the action of alcoholic potassium hydroxide on the bromo-acid, or of barium hydroxide on its ester, Δ^5 -*campholytic acid* is produced, which crystallises in needles, melts at 90—91°, and decolorises a potassium permanganate solution; when warmed with dilute sulphuric acid, it is not converted into β -campholytic acid. Δ^5 -*Campholytic amide* crystallises in leaflets or small plates, and melts at 90°. E. G.

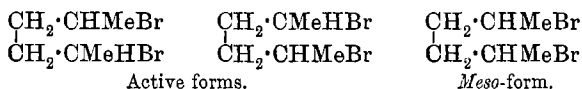
2:5-Dimethyl-1:1-Di- and -1-Mono-Carboxylic Acids of cyclopentane. By JOHANNES WISLIGENUS [with KURT PETERS, OTTO SCHRAMM, and OTTO MOHR] (*Ber.*, 1901, 34, 2565—2583).—When β -dibromohexane (Schramm, *Abstr.*, 1897, i, 262), boiling at 99—100° under 20 mm. pressure, is suspended in boiling alcohol, mixed with a slight deficiency of ethyl disodiummalonate, and heated until the mixture has become neutral in reaction, an oil is obtained boiling at 169—180° under 76 mm., or at 250—264° under the ordinary pressure, and with the composition of diethyl dimethylcyclopentanedicarboxylate. When this is hydrolysed with 20 per cent. alcoholic potash, a mixture of ester-acids, dicarboxylic acids, and monocarboxylic acids is obtained; these can be

separated by means of their different solubility in light petroleum or water, or different volatility with steam. Each of them was shown to be related to one or other of two dicarboxylic acids, and the original ester must have been a mixture of the diethyl esters of these two acids; the pure esters were prepared by starting with the acids. The acids are stereoisomerides, being derived from stereoisomeric dimethylcyclopentanes in which the two methyl groups are respectively on the same side (*cis-cis*), and on opposite sides (*cis-trans*), of the pentamethylene ring, as is indicated by the formulæ



They were identified by eliminating one carboxyl group from each by heating it at 190–210°. Under these circumstances, one of them yielded two (stereoisomeric) monocarboxylic acids, the other only one; it is obvious from the formulæ that these must have been the *cis-cis* and *cis-trans*-dicarboxylic acids respectively.

The $\beta\epsilon$ -dibromohexane employed can be separated into a solid and a liquid part by cooling it to 0° and inoculating it with a crystal of the solid, obtained by cooling a small portion with solid carbon dioxide and ether (compare Demjanoff, Abstr., 1891, 160). The solid $\beta\epsilon$ -dibromohexane melts at 38.2°, boils at 98–99° under 16–17 mm. pressure, and has a sp. gr. 1.5315 at 56°. The liquid isomeride, when purified as far as possible, boiled at 94° under 13–14 mm. pressure, and had the sp. gr. 1.5256 at 56°, and 1.5822 at 11.9°. Now it is possible, theoretically, for $\beta\epsilon$ -dibromohexane to exist in several stereoisomeric forms, as the following formulæ indicate:—



When the condensation with ethyl disodiummalonate takes place, the two bromine atoms which are eliminated will presumably take up positions opposite to each other. In the case of the *meso* form, this will bring the two methyl groups to the same side of the pentamethylene ring which is formed, and so would give rise to a *cis-cis*-dimethylcyclopentane derivative. In the case of either of the two active forms, the two methyl groups will be brought to opposite sides of the ring, with consequent formation of a *cis-trans*-derivative. By actual experiment, it is found that the solid dibromohexane gives *cis-cis*-dimethylcyclopentane derivatives, and so it must possess the *meso*-configuration. On the other hand, the liquid isomeride gives *cis-trans*-derivatives, and must therefore be regarded as a racemic mixture of the active forms.

The following new compounds were prepared:—

cis-cis-2 : 5-Dimethylcyclopentane derivatives.—1 : 1-Dicarboxylic acid, $\text{C}_5\text{H}_8\text{Me}_2(\text{CO}_2\text{H})_2$, melting and decomposing at 192–194°; silver salt; calcium salt, with $6\text{H}_2\text{O}$; diethyl ester, boiling at 138° under 20 mm.

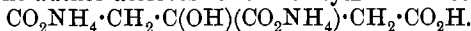
pressure, with a sp. gr. 1.019. The acid, when heated, yields two 1-monocarboxylic acids, $C_5H_7Me_2 \cdot CO_2H$, melting at $26-30^\circ$ (silver salt analysed), and $75-77^\circ$ (silver salt and calcium salt, with $2H_2O$, analysed). The ester, when hydrolysed, yields mainly an ester-acid, $CO_2Et \cdot C_5H_7Me_2 \cdot CO_2H$, melting at 81.5° ; silver salt analysed. This yields, when heated, an ethyl 1-carboxylate, $C_5H_7Me_2 \cdot CO_2Et$, which boils at $187-188^\circ$, has a sp. gr. 0.920, and can be hydrolysed to the monocarboxylic acid melting at $75-77^\circ$.

cis-trans-2 : 5-Dimethylpentane derivatives.—1 : 1-Dicarboxylic acid, melting and decomposing at $204-205^\circ$; silver salt; calcium salt, with $\frac{1}{2}H_2O$; yields, on esterification, the diethyl ester, boiling at 133° under 20 mm. pressure and with a sp. gr. 1.022, and the ester-acid, which melts at 54° (silver salt analysed), and, when heated, yields the ethyl 1-carboxylate. This boils at 190° , has a sp. gr. 0.926, and can be hydrolysed to the 1-carboxylic acid, which is also formed when the dicarboxylic acid is heated. This acid melts at $49-50^\circ$; its silver salt and calcium salt, with $1H_2O$, were analysed. C. F. B.

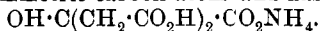
Rubidium Racemate. By GRÉGOIRE N. WYROUBOFF (*Chem. Centr.*, 1901, ii, 764; from *Bull. Soc. franç. Min.*, 1901, 24, 270—273. Compare *ibid.*, 6, 58, and Traube, *Jahrb. Min.*, [ii], *Beilageband*, 10, 795).—Rubidium racemate, $C_4H_4O_6Rb_2 \cdot 2H_2O$, crystallises at temperatures below 20° in large, monoclinic plates [$a : b : c = 0.9024 : 1 : 0.6323$; $ac = 91^\circ 42'$]. E. W. W.

Constitution of Citric Acid Derivatives. By GUIDO SCHIAVON (*Gazzetta*, 1901, 31, i, 536—544).—The author has prepared various salts by partially or completely neutralising citric acid with a base or with two bases in the proportion of two equivalents of the one to one of the other, the salts obtained being examined, especially as regards their crystalline form and rotatory power, with the view of elucidating their constitution.

The diammonium hydrogen salt separates from its concentrated solution in crystals melting at 150° . [PANEBIANCO finds that these crystals occur only in dextro-hemihedral forms and not in equal proportions of the dextro- and lævo-forms as was stated by Heusser.] The solution of these crystals is optically inactive, but after the action of *Penicillium glaucum* in presence of nutritive salts, it becomes slightly lævorotatory. The monoclinic form of this salt, described by Heldt in 1843, could not be prepared. The diammonium salt is obtained in deliquescent rhombic crystals containing $\frac{1}{2}H_2O$ when powdered citric acid is neutralised with concentrated ammonia solution. On account of the optical activity conferred on this salt by *Penicillium*, the author ascribes to it the asymmetric formula,

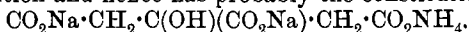


The monoammonium dihydrogen salt separates from its solution in triclinic, deliquescent crystals, the solution of which is optically inactive and remains so after the action of *Penicillium*. The salt hence probably contains no asymmetric carbon atom and has the formula



The disodium monoammonium salt, obtained either by neutralising monoammonium citrate with sodium carbonate or by neutralising two-thirds of a given quantity of citric acid with sodium carbonate and

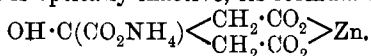
the remaining third with ammonia, is slightly laevorotatory in concentrated solution and hence has probably the constitution



The disodium salt from which the last-named is formed must therefore have the formula $\text{CO}_2\text{Na}\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{CO}_2\text{Na})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

By the addition of citric acid to the neutral optically inactive trisodium salt, a disodium hydrogen citrate is obtained, which is also optically inactive and has the constitution $\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{Na})_2\cdot\text{CO}_2\text{H}$.

The dizinc monoammonium salt, formed by the action of ammonia on the trizinc compound, is obtained as a white, insoluble deposit containing $2\text{H}_2\text{O}$ and is optically inactive, its formula being



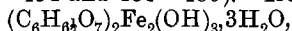
Examination of the behaviour of citric acid towards indicators gave the following results. Litmus, phenolphthalein, rosolic acid, and tropæolin-OOO indicate neutrality when the three carboxylic hydrogen atoms of citric acid have been replaced. Cochineal and congo-red are neutral towards salts containing one unreplaced carboxylic hydrogen, whilst tropæolin-OO has a neutral reaction with citrates, in which only one-third of the carboxylic hydrogen has been replaced; methyl-orange apparently acts like tropæolin-OO, but does not lend itself well to use with citric acid. Lacmoid behaves similarly to the indicators given in the first group above, but when the acid solution is neutralised to the extent of two-thirds, it assumes a more violet colour with a red fluorescence.

T. H. P.

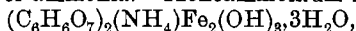
[Manganese Citrate.] By FREDERICK B. POWER (*Pharm. J.*, 1901, [iv], 13, 135—137).—Manganese citrate, $\text{Mn}_3(\text{C}_6\text{H}_5\text{O}_7)_2\cdot 9\text{H}_2\text{O}$, was first prepared by Kammerer (*Annalen*, 1868, 148, 314) by heating together solutions of manganous acetate and citric acid. The author has obtained the same salt by the action of citric acid on manganous carbonate.

E. G.

Iron Citrate and Iron Ammonium Citrate. By C. MARTINOTTI and L. CORNELIO (*Chem. Centr.*, 1901, ii, 626, 764; from *Boll. Chim. Farm.*, 1901, 40, 445—454 and 481—489).—Iron citrate,



cannot be regarded as a normal citrate since it has an acid reaction, loses $3\text{H}_2\text{O}$ at 100° , is completely dehydrated only at 150° , and combines with 3 mols. of ammonia. Monoammonium iron citrate,



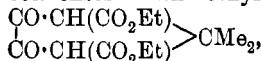
prepared in the same way as the diammonium salt and also by the oxidation of the corresponding ferrous ammonium citrate, is very slightly deliquescent and far less soluble than the di- and tri-ammonium salts. The diammonium salt, $(\text{C}_6\text{H}_5\text{O}_7)_2(\text{NH}_4)_2\text{Fe}_2(\text{OH})_3\cdot 3\text{H}_2\text{O}$, is browner than the monoammonium iron citrate. The triammonium salt, $(\text{C}_6\text{H}_5\text{O}_7)_2(\text{NH}_4)_3\text{Fe}_2(\text{OH})_3\cdot 3\text{H}_2\text{O}$, is prepared by treating iron citrate with ammonia until it shows an alkaline reaction.

The green iron ammonium citrate, obtained by adding ammonium citrate or citric acid to the reddish-brown iron triammonium citrate, is really a mixture of iron citrate, $(\text{C}_6\text{H}_5\text{O}_7)_2\text{Fe}_2$, with ammonium

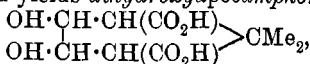
citrate and usually also with citric acid. Ferrous citrate, $C_6H_6O_7Fe, H_2O$, is a greenish-white powder and dissolves very readily in ammonia with a slight development of heat, forming a rather unstable ferrous ammonium citrate, $C_6H_5O_7(NH_4)Fe$, which is easily oxidised to diammonium ferric citrate.

E. W. W.

Complete Synthesis of apoCamphoric Acid (Camphopyric Acid). By GUSTAV KOMPPA (*Ber.*, 1901, **34**, 2472—2475).— $\beta\beta$ -Dimethylglutaric acid (*Abstr.*, 1899, i, 573) condenses with ethyl oxalate to form *ethyl diketoapocamphorate*,



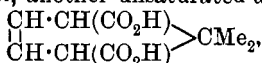
which melts at 98° ; the analogous *methyl* ester melts at 115 — 116° . On reduction, the acid yields *dihydroxyapocamphoric acid*,



which is converted by hydriodic acid into an unsaturated *acid*, probably

$$\begin{array}{c} \text{CH}\cdot\text{C}(\text{CO}_2\text{H}) \\ | \\ \text{CH}\cdot\text{C}(\text{CO}_2\text{H}) \end{array} > \text{CMe}_2,$$

melting at 203 — 209° ; when this is reduced with sodium and amyl alcohol, another unsaturated *acid*,



is obtained, which forms triclinic tablets, melts at 203 — 205° , and yields, with hydrobromic acid at 120 — 130° the *additive* compound

$$\begin{array}{c} \text{CHBr}\cdot\text{CH}(\text{CO}_2\text{H}) \\ | \\ \text{CH}_2\text{—CH}(\text{CO}_2\text{H}) \end{array} > \text{CMe}_2.$$

The latter, on reduction with zinc dust and

acetic acid, gives apo- or nor-camphoric acid,

$$\begin{array}{c} \text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H}) \\ | \\ \text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H}) \end{array} > \text{CMe}_2,$$

melting at 160 — 170° , and identical with *mesocamphopyric acid* (Marsh and Gardner, *Trans.*, 1896, **69**, 79). The acid was resolved into its *cis*- and *trans*-forms, and the *cis*-form identified by its melting point (203.5 — 204.5°), and that of its anhydride (174 — 175°) and anil (211°). This synthesis confirms Bredt's formulæ for camphor, camphene, and fenchocamphorone.

W. A. D.

Molecular Weight of Chloral Hydrate at the Boiling Point. By ROBERT DE FORCRAND (*Compt. rend.*, 1901, **133**, 474—476).—If Berthelot's values of 21900 cal. and 5500 cal. be adopted for the molecular heats of evaporation and fusion of chloral hydrate, the value of $(L+S)/T$ is 74.1, in place of the usual constant 30. If the compound were completely dissociated, the value 60 should be obtained. The values given for the latent heats, however, include the heat of combination, 6230 cal., and by subtracting this from $L+S$, the quotient $(L+S)/T$ is 57.3. This indicates almost complete dissociation and by the converse calculations, adopting the value 30 for the constant, the value 86.6 is obtained for the molecular weight, 82.75 corresponding with complete dissociation. As the constants for water are accurately known, the author attempts further to separate the calculation into two parts, (1) that due to water, (2) that due to the chloral, and so obtain the value 31.4 for $(L+S)/T$ in the case of the anhydrous compound. Although the results can only be approxi-

mate, they indicate 4 or 5 per cent. of undissociated hydrate at the boiling point (this vol., ii, 372, 594). L. M. J.

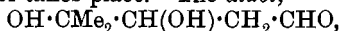
Researches on the Acetals. By MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1901, [vii], 23, 378—416 and 482—498).—A detailed account of work already published (compare this vol., i, 3, 254, 314, 365; ii, 6). G. T. M.

Action of Barium Hydroxide and of Sodium on several Aldehydes. By ANTON LÆDERER (*Monatsh.*, 1901, 22, 536—544).—Barium hydroxide converts acetaldehyde and crotonaldehyde in aqueous solution into resins. *iso*Butaldehyde, when heated in a sealed tube with barium hydroxide and a small quantity of water, is transformed nearly quantitatively into *isobutyl* alcohol and *isobutyric* acid. The formation of an alcohol and acid from an aldehyde (Cannizzaro's reaction) has never been previously observed in the case of an aldehyde in which hydrogen is attached to the α -carbon atom (compare Lieben, this vol., i, 449). On treating *isovaleraldehyde* with barium hydroxide, α -*isopropyl*- β -*isobutyl*acraldehyde is formed (Kohn, Abstr., 1896, i, 461).

Metallic sodium (or sodium hydroxide) converts *isobutaldehyde* mainly into octoglycol *isobutyrate* (Brauchbar and Kohn, Abstr., 1898, i, 353), a small quantity of *isobutyl* alcohol being formed at the same time. *iso*Valeraldehyde is transformed by metallic sodium into an ester of *isovaleric* acid and the glycol $C_{10}H_{22}O_2$ (see following abstract). K. J. P. O.

Condensation Products of *iso*Valeraldehyde. By HUGO ROSINGER (*Monatsh.*, 1901, 22, 545—560).—*iso*Valeraldehyde was found by Kohn (Abstr., 1896, i, 461, and 1897, i, 396) to form three condensation products, an unsaturated aldehyde, *isovaleraldol*, and a compound $(C_5H_{10}O)_x$ to which Reychler (Abstr., 1897, i, 549) assigned the formula $C_{10}H_{20}O_2$. The author finds that this substance is best prepared by boiling the aldehyde with solid potassium hydroxide and has the formula $C_{15}H_{20}O_3$. It is the ester of *isovaleric* acid and the glycol $C_{10}H_{22}O_2$; the latter is obtained by hydrolysing the ester with alcoholic potash and is a viscous oil boiling at 143° under 15 mm. pressure; it yields a *diacetate*, $C_{10}H_{20}O_2Ac_2$, as an oil boiling at 145° under 18 mm. pressure. When heated with acetic anhydride, the ester yields no acetyl derivative, but when treated with acetic anhydride and sulphuric acid, it gives a *monoacetate*, $C_{15}H_{20}O_3Ac$, which is an oil boiling at 150° under 18 mm. pressure. For the ester, the author suggests the constitution $CH_2Pr^\beta \cdot CO_2 \cdot CH_2 \cdot CHPr^\beta \cdot CH(OH) \cdot CH_2Pr^\beta$. K. J. P. O.

Condensation of α -Hydroxybutaldehyde with Acetaldehyde. By JULIUS ROESLER (*Monatsh.*, 1901, 22, 527—535).—When a mixture of α -hydroxyisobutaldehyde and acetaldehyde in molecular proportion is left in contact with 3*N* potassium hydroxide for three weeks, condensation to an aldol takes place. The aldol,



boils at 125 — 127° under 16 mm. pressure, and can be obtained in white crystals melting gradually at 70° . It reduces ammoniacal silver

nitrate, and on distillation at the ordinary pressure is converted into an unsaturated aldehyde. The *diacetate*, $C_6H_{10}O_5Ac_2$, is an oil boiling at 140° under 16 mm. pressure; the *oxime*, $C_6H_{13}O_3N$, is an oil. On reducing the aldol with aluminium amalgam, an oil was obtained which could not be purified; it yields a *diacetate*, $C_6H_{12}O_5Ac_2$, which is an oil boiling at $162-164^\circ$ under 16 mm. pressure, and is probably the diacetate of a hexylglycerol.

K. J. P. O.

Compounds of the Alkali Metals and Cyclic Aminoketones. EMANUEL MERCK (D.R.-P. 119506).—Tropinone, triacetoneamine, and vinyl diacetoneamine suspended in dry ether or benzene yield sodium or potassium derivatives on treatment with the metal in the form of wire or ribbon. These products form yellow, hygroscopic powders, and are immediately decomposed by water, regenerating the aminoketones.

G. T. M.

$\beta\gamma\delta$ -Triketopentane. I. By FRANZ SACHS and HERMANN BARSCHALL (*Ber.*, 1901, **34**, 3047—3054).—*Diacyetyl-4-dimethylaminophenylazomethine* (*triketopentane- γ -p-dimethylaminoanil*), $NMe_2 \cdot C_6H_4N : CAc_2$, obtained by condensing acetylacetone with nitrosodimethylaniline in alcoholic solution in the presence of sodium hydroxide, and cooling the product to -20° , crystallises from light petroleum in orange-yellow crystals, and melts at 73° ; it is very soluble in the other organic solvents, and has a yellow vapour.

$\beta\gamma\delta$ -Triketopentane hydrate, $COMe \cdot C(OH)_2 \cdot COMe$, is prepared by hydrolysing the preceding compound with 10 per cent. sulphuric acid, extracting the product with ether, distilling the extract under 30 mm. pressure until an orange-yellow oil, *triketopentane*, is obtained, and allowing this to take up moisture by exposure to the atmosphere; it forms well-defined, colourless, rhombic prisms melting indefinitely from $32-50^\circ$. This hydrate crystallises from benzene without losing the elements of water, and is readily soluble in the other organic solvents with the exception of light petroleum; it slowly decomposes and becomes liquid when kept in a desiccator. It reduces potassium permanganate in the cold without producing a precipitate of the dioxide; ammoniacal silver nitrate and chromic acid are also readily reduced; Fehling's solution and copper acetate yield cuprous oxide even in the cold, whilst metallic copper is precipitated from a boiling solution of the sulphate. The dihydrate reddens litmus.

$\beta\gamma\delta$ -Triketopentane, $COMe \cdot CO \cdot COMe$, has not hitherto been obtained completely free from the hydrate; it is the first and simplest example of the straight chain consecutive triketones.

Triketopentane bis-phenylhydrazone, $C_5H_6O : (N \cdot NPh)_2$, formed in dilute alcoholic solutions of its generators with or without the addition of acetic acid, crystallises from alcohol in orange needles with a blue reflex and melts at 156° . The *dianil*, $C_5H_6O : (NPh)_2$, is obtained in prisms and melts at 157.5° ; it is somewhat unstable and soon develops an odour of carbimide, whilst the melting point falls.

2 : 3-Acetylmethylquinoxaline, $C_6H_4 \begin{smallmatrix} \diagup N : CAc \\ \diagdown N : CMe \end{smallmatrix}$, or less probably



prepared by the interaction of *o*-phenylenediamine hydrochloride and triketopentane in the presence of sodium acetate, crystallises from alcohol in pale yellow needles and melts at 86.5° ; it dissolves in concentrated sulphuric acid to a deep yellow solution. G. T. M.

Behaviour of Carbohydrates with Hypochlorites. By WALTER BRAEUTIGAM (*Chem. Centr.*, 1901, ii, 680—681; from *Pharm. Zeit.*, 46, 636—638).—When 20 parts of bleaching powder are triturated with 2 of dextrose, the mixture becomes moist, the temperature rises to 125° , steam is given off copiously, and a solid mass consisting of calcium carbonate and calcium oxalate is ultimately obtained. A violent action also occurs when the filtrate from a mixture of 20 parts of bleaching powder with 100 of water is treated with 2 parts of dextrose at 50° and the same products are formed; but when mixed in the cold the temperature rises to about 30° ; the product consists mainly of calcium carbonate, with only a small quantity of oxalate, and a similar result is obtained when dilute solutions of hypochlorite are employed. The carbonic acid may possibly be derived from the decomposition of formic acid. Generally speaking, the members of the glucose and sucrose groups are decomposed by cold concentrated solutions of hypochlorites forming carbon dioxide, oxalic acid, and water, whilst the members of the cellulose and melitose groups are only attacked at 60 — 70° , forming dextrose, which is then decomposed either into carbon dioxide, oxalic acid, and water, or into carbon dioxide and water, according to the concentration of the solution.

E. W. W.

Derivatives of Dextrose and Galactose. By A. COLLEY (*Ber.*, 1901, 34, 3205—3207).—This paper supplements that of Koenigs and Knorr on the same subject (this vol., i, 369). Tetracetyl bromodextrose is best prepared by the action of acetyl bromide on dextrose in a sealed vessel at -10° . Tetracetyl chlorodextrose is converted by silver acetate in acetic acid solution into the pentacetyl dextrose melting at 131° , but with silver sulphate in the same solution it yields the oppositely active pentacetyl dextrose melting at 111.8° .

W. A. D.

Isomeric Acetyl Halogen Derivatives of Dextrose, and the Synthesis of Glucosides. By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Ber.*, 1901, 34, 2885—2900. Compare *Abstr.*, 1894, i, 3; this vol., i, 257).— α -Tetracetyl chlorodextrose is readily transformed into the isomeric β -compound when its ethereal solution is shaken with a little powdered crystallised sodium carbonate.

Heptacetylchloromaltose, $C_{26}H_{35}O_{17}Cl$, obtained by the action of aqueous hydrochloric acid on octacetylmaltose at 15° , forms small, colourless prisms, and melts at 64 — 66° .

Heptacetyl- β -methylmaltoside, obtained when the preceding compound is shaken with methyl alcohol and silver carbonate, crystallises in needles melting at 121 — 122° (corr.), and on hydrolysis with baryta water yields *β -methylmaltoside*, which, so far, has not been obtained in a crystalline form. It dissolves readily in water, but is very sparingly soluble in organic solvents, does not reduce Fehling's solution except after hydro-

lysis with acids, is strongly dextrorotatory, and on treatment with emulsin is converted into maltose, whereas yeast enzyme transforms it into dextrose and β -methylglucoside.

Tetracetyl- β -phenylglucoside, $C_{20}H_{24}O_{10}$, obtained by the action of sodium phenoxide (2 mols.) on β -tetracetylchlorodextrose, crystallises from alcohol in large, prismatic needles, melts at 127° (corr.), has a bitter taste, is very sparingly soluble in water, and has $[\alpha]_D -29.04^\circ$ at 20° . On hydrolysis with baryta water, it yields β -phenylglucoside which has $[\alpha]_D -71.0^\circ$ at 20° (compare Michael, *Amer. Chem. J.*, 1879, i, 307).

Tetracetyl- β -naphthylglucoside, $C_{24}H_{26}O_{10}$, crystallises in needles melting at $135-136^\circ$ (corr.). J. J. S.

Measurement of the Rotatory Power of Sugar, its Variation with Temperature and with the Wave-length of the Light used. By HENRI PELLAT (*Ann. Chim. Phys.*, 1901, [vii], 23, 289—316).—The quantity of sugar required to be dissolved to give 100 c.c. of solution at 20° , which in a 20 cm. tube (at 20°) rotates the plane of polarisation of the sodium D line through 21.67° , is 16.284 grams (or, corrected for the amount of ash left by the sugar examined, 16.275 grams). This gives for the specific rotation, $[\alpha]_D$, 66.536° at 20° , which is almost identical with the value (66.538°) reported by Mascart and Bénard to the *Commission pour l'unification des méthodes d'analyse des alcools et des sucres*. The variation of the rotation (measured in a glass tube) with the temperature, between 14° and 30° , is expressed by $\alpha_D^{20} = \alpha_D^t [1 + 0.00037 (t - 20)]$. For the determination of the variation with the wave-length, the bright lines of various metals produced by the analysis of an arc light by the spectroscope were used. From the results obtained, it is clear that these cannot be represented by the inverse ratio of the squares of the wave-lengths, but the rotation for any particular wave-length can be found from the formula $\alpha_\lambda = \alpha_D (A/\lambda^2 + B/\lambda^4)$, where λ is the wave-length, and $A = 0.325483$, and $B = 0.00757003$, α_D , the rotation for the sodium D line, being accurately known. J. McC.

Mixed Esters of Cellulose and the Behaviour of Cellulose towards Nitrating Acids. By CHARLES F. CROSS, EDWARD J. BEVAN, and R. LEONARD JENKS (*Ber.*, 1901, 34, 2496—2499).—Contrary to the generally accepted view that the sulphuric acid used in nitrating cellulose exercises a merely dehydrating influence, it is shown that the acid initially combines with the fibre simultaneously with the nitric acid to form a mixed nitrate-sulphate; after the product is washed with cold water until the washings are neutral, it contains considerable quantities of combined sulphuric acid, the proportion of the latter diminishing with the time of nitration, and especially with the percentage of water present in the nitrating mixture. When the nitration lasted only 7 minutes, and a mixture of sulphuric and nitric acids in the proportion 3 : 1 was used, no water being present, the product contained 4.62 per cent. of sulphuric acid; with 10.13 per cent. of water present, the percentage of combined sulphuric acid was only 2.56.

The sulphuric groups present are largely removed by hydrolysis

when the cellulose nitrate is purified by boiling with water, and also by means of acetone containing sufficient water to prevent its acting as a solvent.

W. A. D.

Researches on Caramel. IV. Decomposition Products of Caramelan. By FERDINAND STOLLE (*Zeit. Ver. deut. Zuckerind.*, 1901, 836—838).—One hundred grams of caramelan were heated for 18 hours on the water-bath with 1 litre of 3 per cent. hydrochloric acid, the products being 30 grams of a brownish-red, insoluble substance, and a hexose which gives an osazone crystallising in spherical aggregates of yellow needles melting at 197°, but which has not yet been identified.

T. H. P.

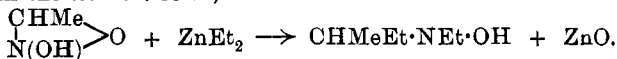
A Trimethyltriose. By CARL D. HARRIES and PAPPAS (*Ber.*, 1901, 34, 2979—2980).—A *trimethyltriose* (*dihydroxydihydromesityl oxide*), $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{COMe}$, is obtained as an oil on oxidising mesityl oxide, suspended in acetone, with cold potassium permanganate solution (Sachs, this vol., i, 272), and saturating the filtered and concentrated aqueous extract with potassium carbonate; it boils at 109° under 19 mm. pressure, and has a sp. gr. 1.077 at 22°. The new triose is a pale yellow, syrupy liquid having an odour of burnt sugar; it reduces Fehling's solution even in the cold, and dissolves in the ordinary organic solvents. The yield is 60 per cent. of the theoretical. The substance readily decomposes into acetone and acetol even on distillation under reduced pressure, the fraction obtained between 50—100° under 20 mm. pressure yielding acetol semicarbazone with semicarbazide, and the osazone of methylglyoxal with phenylhydrazine.

G. T. M.

Action of Hydrogen Peroxide on Fatty Amines. II. By LEONARD MAMLOCK and RICHARD WOLFFENSTEIN (*Ber.*, 1901, 34, 2499—2505. Compare Abstr., 1900, i, 209).—Tripropylamine oxide is formed by the propylation of either β -dipropylhydroxylamine or of hydroxylamine with propyl iodide and sodium propyloxide (compare Dunstan and Goulding, *Trans.*, 1899, 75, 793); when prepared by the action of hydrogen peroxide on tripropylamine, it is obtained in the form of a crystalline hydrate, $\text{NPr}_3^a(\text{OH})_2$, which only loses its combined water on complete decomposition. The oxide is reduced by sulphur dioxide in hot aqueous solution to tripropylamine, but at 0° is

converted into *N-hydroxytripropylsulphamic anhydride*, $\text{NPr}_3^a\text{SO}_2\text{O}$, which separates in white, silky crystals, melts at 159°, and is also obtained by the action of sulphur trioxide on tripropylamine at 0°. Dipropylsulphamic acid, formerly obtained by the action of sulphur dioxide on dipropylhydroxylamine, is also formed by the decomposition with boiling water of the *chloride*, $\text{NPr}_2^a\cdot\text{SO}_2\text{Cl}$, produced by the action of sulphuryl chloride on dipropylamine.

The formation of β -ethyl*sec.*butylhydroxylamine from nitroethane and zinc ethyl (Bewad, *Abstr.*, 1900, i, 629) is due to the former inter-acting in the *isonitro*-form, thus:



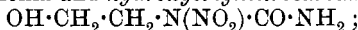
Bewad's base yields, with sulphur dioxide in benzene solution, the amorphous *ethylsec. butylsulphamic acid*, $C_4H_9 \cdot N\text{Et} \cdot SO_2 \cdot OH$, which melts at 89—93°. The formation of this confirms Bewad's view as to the nature of the base.

W. A. D.

New Class of Nitroamines. By ANTOINE P. N. FRANCHIMONT [with LUBLIN] (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 88—91. Compare Abstr., 1895, i, 445).—Aminoethyl alcohol combines with methyl chloroformate, producing *methyl hydroxyethylaminoformate*, $OH \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO_2Me$, which is a colourless liquid, decomposing, on heating, into methyl alcohol and the internal anhydride of hydroxyethylaminoformic acid. The *ethyl* ester is a liquid which does not decompose on heating, and can be distilled under reduced pressure.

On treating hydroxyethylaminoformic anhydride (2-ketotetrahydro-oxazole) with pure nitric acid, a stable *mononitro*-derivative is obtained, crystallising in long, lustrous needles and melting at 111°. When boiled with water, it decomposes quantitatively into carbon dioxide and *nitroaminoethyl alcohol*, $NO_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot OH$, which is obtained as a syrupy liquid on evaporating the aqueous solution; with boiling dilute sulphuric acid, it yields glycol and nitrous oxide. The *mercury* salt, prepared by boiling an aqueous solution of the nitroamine with mercuric oxide, crystallises in needles; the *silver* salt, similarly prepared, in plates; both salts explode on heating.

By the action of dry ammonia on a benzene solution of the internal anhydride, a compound is obtained, which, when boiled with absolute alcohol, yields ammonia and *hydroxyethylnitrocarbamide*,



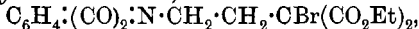
this substance crystallises in glossy plates, melting at 86°, and in aqueous solution, gives a white precipitate with mercuric nitrate; with barium hydroxide, it decomposes into nitroaminoethyl alcohol, ammonia, and carbon dioxide. The above carbamide derivative can be titrated with potassium hydroxide in the presence of phenolphthalein, and behaves as a monobasic acid.

K. J. P. O.

Detection of Amino-derivatives of Sugars. I. By H. STEUDEL (*Zeit. physiol. Chem.*, 1901, 33, 223—224).—Phenylcarbimide (Paal, Abstr., 1894, i, 332) is recommended as a precipitant for amino-derivatives of sugars. With glucosamine, it yields a *product*, $C_{13}H_{16}O_5N_2$, which is deposited from dilute acetic acid in the form of large, rhombic crystals, turning brown at 200° and melting sharply at 210°.

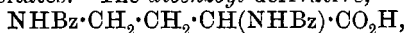
J. J. S.

Synthesis of α -Diaminobutyric Acid. By EMIL FISCHER (*Ber.*, 1901, 34, 2900—2906. Compare this vol., i, 191).—*Ethyl β -phthaliminoethylbromomalonate*,



obtained by the action of bromine on a chloroform solution of crude ethyl β -phthaliminoethylmalonate (Abstr., 1891, 1247) in sunlight, crystallises from alcohol, when cooled to -20°, in colourless, truncated prisms, melts at 76—78°, and decomposes at 220—230°. After hydrolysis with hydrobromic acid saturated at 0°, and subsequent heating at 140—150° for 45 minutes, it yields a *bromo γ -phthaliminobutyric*

acid; this crystallises in colourless plates, melts at 154—156° (corr.), and is readily soluble in most organic solvents. When treated with anhydrous liquid ammonia or, better, with aqueous ammonia, it yields *α-amino-γ-phthaliminobutyric acid*, which crystallises from hot water in small plates melting and decomposing at about 197°. On hydrolysis with hydrochloric acid of sp. gr. 1.19 at 100°, the phthalimino-acid yields *α-γ-diaminobutyric acid hydrochloride*. The *acid* is extremely hygroscopic and readily soluble in water, but only sparingly so in alcohol, ether, or light petroleum. Its aqueous solution has a strong alkaline action and readily absorbs carbon dioxide. The normal *oxalate*, $(C_4H_{10}O_2N_2)_2 \cdot C_2H_2O_4 \cdot 2H_2O$, crystallises in large, colourless plates, and melts and decomposes at about 219°. The *nitrate*, *sulphate*, *hydrochloride*, and *platinichloride* are all readily soluble, the *aurichloride* is readily decomposed, and the phosphotungstate and mercurichloride form white precipitates. The *dibenzoyl* derivative,

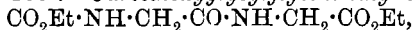


is formed when a considerable excess of benzoyl chloride is employed, and crystallises in small needles melting at 200—201°.

J. J. S.

Derivatives of Glycine. By EMIL FISCHER and ERNEST FOURNEAU (*Ber.*, 1901, 34, 2868—2877).—This paper deals with molecular anhydrides of amino-acids as distinct from the bimolecular anhydrides or diacipiperazines, and in it the name *glycyl* is used for the radicle $NH_2 \cdot CH_2 \cdot CO$.

Glycylglycine hydrochloride, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H, HCl, H_2O$, crystallises out as a mass of slender needles when glycine anhydride (diacipiperazine) is dissolved in and boiled for a minute with strong hydrochloric acid; when treated with aqueous alkalis, or, better, with moist silver oxide, it is converted into *glycylglycine*, which crystallises in lustrous leaflets and decomposes between 215° and 220°. The following derivatives of *glycylglycine* are described: a deep blue *copper* salt crystallising in needles; the *ethyl* ester, which crystallises from light petroleum in slender needles melting at 88—89° (corr.), and in aqueous solution rapidly regenerates the glycine anhydride at the ordinary temperature; the *hydrochloride* of the ester, which crystallises in lustrous needles, and melts and decomposes at 182° (corr.); and the *phenylcarbimide*, $NHPh \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, which crystallises from water in slender, silky needles, melts and decomposes at 175° (corr.), and forms a crystalline *ethyl* ester, $C_{13}H_{17}O_4N_3$, melting at 165—166°. *Carbethoxyglycylglycine ethyl ester*,

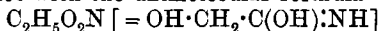


obtained by the action of ethyl chlorocarbonate on *glycylglycine ethyl ester*, crystallises from ethyl acetate in flat prisms, dissolves readily in hot water, alcohol, or benzene, melts at 87° (corr.), and when treated with liquid ammonia at the ordinary temperature or with alcoholic ammonia at 100° yields *carbamidoglycylglycine ethyl ester*, $C_7H_{13}O_4N_3$, which crystallises from alcohol or water in six-cornered leaflets, melts and decomposes at 183° (corr.), and gives the biuret reaction.

Similar compounds can be obtained from the ethyl ester of leucine and from alanine anhydride.

R. H. P.

The so-called *isoAmides* and *True Amides*. By ARTHUR HANTSZCH and E. VOEGELEN (*Ber.*, 1901, **34**, 3142—3163).—Determinations of the molecular weight of glycolliminohydrin by the boiling point method, using absolute alcohol as solvent, agree with the formula $C_4H_{10}O_4N_2$, and not with the unimolecular formula



(compare Eschweiler, *Abstr.*, 1897, i, 399; Steiner, *Diss. Erlangen*, 1897; Plinke, *Diss. Jena*, 1898). Unlike glycollamide, which is not an electrolyte, glycolliminohydrin has a conductivity in aqueous solution corresponding with that of the salts; $\mu_{64} = 67.30$; $\mu_{2048} = 79.50$; $\Delta^{2040-64} = 12.2$. This is due to the dissociation of the molecule $OH \cdot CH_2 \cdot C(:NH) \cdot O \cdot NH_2 \cdot C(OH) \cdot CH_2 \cdot OH$, which is of the ammonium type, into the ions $OH \cdot CH_2 \cdot C(:NH) \cdot O \cdot$ and $OH \cdot CH_2 \cdot C(OH) : NH_2 \cdot$; in presence of sodium hydroxide, the conductivity rapidly and continuously falls, owing to the decomposition of the original double molecule into sodium glycollate and ammonia. The initial value of the conductivity points to the formation of the salt $OH \cdot CH_2 \cdot C(ONa) : NH$, and it is this which then undergoes decomposition; with glycollamide, on the contrary, no such initial salt formation occurs, and the decomposition into sodium glycollate and ammonia is much slower. The depression of the conductivity of a solution of hydrochloric acid by the iminohydrin shows that the formation of the hydrochloride $OH \cdot CH_2 \cdot C(OH) : NH_2Cl$ in solution is incomplete, but the salt can be easily isolated by evaporation; hydrochloric acid causes little decomposition into glycollic acid and ammonia. The true amides, such as glycollamide, acetamide, dimethylacetamide, carbamide, methylcarbamide, tetramethylcarbamide and benzenesulphonamide cause little depression of the conductivity of hydrochloric acid at a dilution v_{32} , and hence do not give rise to salts of the iminohydrin type, $OH \cdot CR : NH_2Cl$.

Whereas glycollamide yields, with acetic anhydride, an *acetyl* derivative, $C_2H_4AcO_2N$, melting at 92° , glycolliminohydrin gives principally a non-crystallisable syrup along with a small quantity of a white, amorphous substance which does not melt at 252° . Glycollamide gives, with bromine in alkaline solution, a *bromoamide*, but glycolliminohydrin gives no definite product. Attempts to obtain the iminohydrin from glycollide and ammonia failed; that the former is not an ammonium salt of the type $ONH_4 \cdot C \begin{smallmatrix} O \cdot CH \\ \diagup \quad \diagdown \\ CH \cdot O \end{smallmatrix} C \cdot ONH_4$ is also shown by the fact that in aqueous solution it does not give the Nessler reaction.

[With MAX BUCHNER.]—Fifteen representative amides of carboxylic and sulphonic acids were found to be neutral in reaction and nearly non-conducting in solution; this was the case even with those containing strongly negative groups, such as the sulphonamides of tribromobenzene and the nitrobenzenes. From the conductivity of the carboxylic amides in sodium hydroxide solution, it appears that they do not give rise to salts in solution; the sodium salts of the sulphonamides exist, however, in solution although more or less hydrolysed, even in the case of tribromo- and dinitro-benzenesulphonamides. Benzene-sulphobenzamide, $PhSO_2 \cdot NHBz$, on the contrary, is a weak acid

and yields a sodium salt, the conductivity of which shows it to be neutral. Acid imides such as phthalimide are very sensitive to sodium hydroxide, and are converted into sodium salts of amino-acids. "Saccharin" is, however, not only a strong and stable acid ($K = 0.387$) yielding stable neutral salts, but is stronger than either *o*- or *p*-sulphaminobenzoic acid ($K = 0.206$ and 0.025 respectively).

Attempts to prepare iminoethers of the type $C_6H_5 \cdot SO(OR) : NH$ by the action of alkyl iodides on the silver derivative of benzene-sulphonamide gave only the alkyl derivatives $C_6H_5 \cdot R \cdot SO_2 \cdot NHR$; the decomposition of the silver or sodium salts of the amides and sulphonamides by hydrogen chloride, cyanide, or sulphide, in absence of water below 0° , gave only the original amides, and not the *iso*-form. The additive compound of benzamide and sodium ethoxide, instead of giving alcohol and the sodium salt, $ONa \cdot CPh : NH$, when heated, underwent complete decomposition. W. A. D.

Spontaneous Conversion of Uric Acid into Carbamide. By TORQUATO GIGLI (*Chem. Zeit.*, 1901, 25, 741).—When dilute solutions of potassium urate are kept for some 2 to 3 years, the urate becomes completely transformed into carbamide and potassium carbonate, probably in accordance with the equation $C_5H_2O_3N_4K + 3H_2O + O_2 = 2CH_4ON_2 + K_2CO_3 + 2CO_2$. J. J. S.

Formation of Berlin Blue and Ferric Hydroxide by the Action of Sunlight on Aqueous Solutions of Potassium Ferricyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, 25, 742—743. Compare this vol., i, 455, 635, 636).—The amounts of ferric hydroxide and of Berlin blue formed depend on the intensity of the illumination and the corresponding differences in temperature. The amounts of Berlin blue form a diminishing arithmetical series when the concentrations of the ferricyanide solutions also form a diminishing arithmetical series. There is always more Berlin blue than ferric hydroxide produced. J. J. S.

Action of Carbon Dioxide on Aqueous Solutions of Ferro- and Ferri-cyanides. By J. MATUSCHEK (*Chem. Zeit.*, 1901, 25, 815).—Carbon dioxide was passed through boiling solutions containing respectively 1 gram of potassium ferrocyanide and 0.7797 gram of potassium ferricyanide in 100 grams of water. The decomposition was complete after 4 days, and in both cases the products were ferric hydroxide, potassium carbonate, and hydrogen cyanide or its decomposition products, ammonia and formic acid. J. J. S.

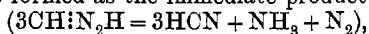
Thiocyanogen, the so-called ψ -Thiocyanogen, and the Yellow Colouring Matter obtained from Thiocyanates. By ALWIN GOLDBERG (*J. pr. Chem.*, 1901, [ii], 64, 166—181. Compare this vol., i, 516).—By the action of hydrogen peroxide or potassium or ammonium persulphate on potassium or ammonium thiocyanate, small quantities of ψ -thiocyanogen are formed. By solution of ψ -thiocyanogen in sulphuric acid and reprecipitation with water, a product is obtained free from oxygen, but still giving all the colour reactions of the original ψ -thiocyanogen, and capable of yielding canarin (*loc. cit.*). K. J. P. O.

Derivatives of isoDiazomethane. By ARTHUR HANTZSCH and MARTIN LEHMANN (*Ber.*, 1901, **34**, 2506—2523).—When a solution of potassium (1 atom.) in ether containing alcohol (2 mols.), or a suspension of sodium ethoxide in ether, is treated at 0° with ethyl diazoacetate, $\text{CO}_2\text{Et}\cdot\text{CH}\begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix}$, amorphous yellow *ethyl potassio-* and *sodio-*iso-

diazoacetate, $\text{CO}_2\text{Et}\cdot\text{C}\begin{smallmatrix} \text{NK} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix}$, and $\text{CO}_2\text{Et}\cdot\text{C}\begin{smallmatrix} \text{NNa} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix}$, $\frac{1}{2}\text{H}_2\text{O}$ are formed respectively. These salts soon decompose spontaneously, even in the dry state; they reduce silver nitrate, mercurous nitrate, and mercuric chloride. When treated with an acid, they yield *ethyl isodiazoacetate*,

$\text{CO}_2\text{Et}\cdot\text{C}\begin{smallmatrix} \text{NH} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix}$; this is an oil which does not dissolve in water, decomposes when distilled, and polymerises when kept to a glassy, brown deliquescent mass that doubtless consists mainly of ethyl bisisodiazoacetate, $\text{CO}_2\text{Et}\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{NH} \end{smallmatrix}\text{C}\cdot\text{CO}_2\text{Et}$, for it yields dihydrotetrazine

(bisisodiazoethane), $\text{CH}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{NH} \end{smallmatrix}\text{CH}$, on prolonged boiling with water. When ethyl isodiazoacetate is treated with hydrochloric acid (as, for instance, when a solution of one of the salts in dilute hydrochloric acid is concentrated on the water-bath), it is decomposed into hydrazine and oxalic acid. Unlike the diazoacetate, it does not form an additive product with sulphites. A solution of an alkali salt in water decomposes spontaneously, alcohol then precipitates a mixture of potassium carbonate and bisdiazoacetate with some bisazoxyacetate. When an aqueous solution of the sodium salt is distilled, isodiazoethane is not obtained, as might be hoped, neither is Curtius's "third isomeride" of similar composition (*Abstr.*, 1889, 371) formed. This substance does not exist; a mixture of hydrocyanic acid and ammonia is really obtained, doubtless from the decomposition of isodiazoethane formed as the immediate product



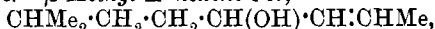
and this mixture was mistaken for a single, new substance. Nor is such a substance formed when an alkali diazoacetate is distilled with water, provided that the salt be pure. But when ethyl diazoacetate is boiled with an aqueous alkali and the product distilled, although the main product is a bisdiazoacetate, yet the distillate contains hydrocyanic acid and ammonia, so that a certain amount of isomerisation (into isodiazoacetate) must have taken place.

A convenient way of preparing potassium diazoacetate, $\text{CO}_2\text{K}\cdot\text{CH:N}_2$, is described. Ethyl diazoacetate (1 mol.) is shaken with 15 per cent. aqueous potassium hydroxide (1 mol.) until solution has been effected, and then alcohol and ether are added; an oil separates from which yellow needles crystallise when it is allowed to remain. Warming with strong aqueous potassium hydroxide polymerises this salt to the bisdiazoacetate, $\text{CO}_2\text{K}\cdot\text{CH:N}_4\cdot\text{CH}\cdot\text{CO}_2\text{K}$. In the same way, diazomethane, $\text{CH}_2\cdot\text{N}_2$, polymerises in ethereal solution to bisdiazomethane, $\text{CH}_2\cdot\text{N}_4\cdot\text{CH}_2$, when exposed to sunlight.

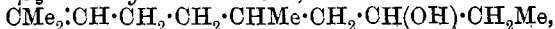
C. F. B.

Mixed Organomagnesium Compounds and their Application to the Synthesis of Acids, Alcohols, and Hydrocarbons.

By VICTOR GRIGNARD (*Chem. Centr.*, 1901, ii, 622—625; from *Ann. Univ. Lyon*, 1901, No. 6, 1—116. Compare *Abstr.*, 1900, i, 382, and this vol., i, 250, 263, 316, and 393).—The organomagnesium compounds, RMgI and RMgBr , prepared by the action of magnesium on the alkyl haloids in ether, contain ether of crystallisation which may be removed by prolonged heating at 150° in a vacuum. Magnesium methiodide decomposes at 255° and magnesium ethobromide at $200\text{--}300^\circ$, forming ethane and ethylene. When carbon dioxide is passed into an ethereal solution of an organomagnesium compound and the precipitate, $\text{R}\cdot\text{CO}_2\cdot\text{MgX}$, decomposed by ice and dilute sulphuric acid, the corresponding acid is formed. Acetic, isovaleric, and isohexoic acids have been prepared by this method. By the action of magnesium methiodide on acetaldehyde, isopropyl alcohol is obtained. Diisobutylcarbinol, from isovaleraldehyde and magnesium isobutylbromide, boils at $113\text{--}115^\circ$ under 87 mm. pressure, has the sp. gr. 0.8237 at 0° , 0.8155 at $12^\circ/4^\circ$ and n_D 1.42629 at 12° . The acetate has a fruity odour and boils at $122\text{--}123^\circ$ under 88 and at 183° under 750 mm. pressure. Δ^2 -pentene- δ -ol, $\text{CHMe}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{OH}$, from crotonaldehyde and magnesium methiodide, boils at $79\text{--}80^\circ$ under 150, at $120\text{--}122^\circ$ under 735 mm. pressure, has the sp. gr. 0.8506 at 0° , 0.8428 at $9.4^\circ/4^\circ$, and n_D 1.43362 at 9.4° . The acetate boils at $136\text{--}137^\circ$ under 751 mm. pressure. γ -Methyl- Δ^7 -hexene- β -ol, $\text{OH}\cdot\text{CHMe}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\text{Me}$, from methylethylacraldehyde and magnesium methiodide, boils at 89° under 55 mm. pressure, has the sp. gr. 0.8768 at 0° , 0.8678 at $9.5^\circ/4^\circ$, and n_D 1.44874 at 9.5° . The acetate boils at $95\text{--}97^\circ$ under 50 mm. pressure. β -Methyl- Δ^5 -hexene- ϵ -ol,



from crotonaldehyde and magnesium isoamylbromide, boils at $89\text{--}91^\circ$ under 11 mm. pressure, has the sp. gr. 0.8600 at 0° , 0.8539 at $9^\circ/4^\circ$, and n_D 1.44713 at 9° . The acetate boils at $96\text{--}98^\circ$ under 13 mm. pressure. $\beta\zeta$ -Dimethyl- Δ^8 -decene- θ -ol,



from citronellal and magnesium ethobromide, has a pleasant odour of lemons, boils at $113\text{--}116^\circ$ under 8 mm. pressure, has the sp. gr. 0.8740 at 0° , 0.8655 at $12.3^\circ/4^\circ$, and n_D 1.46123. The acetate boils at $120\text{--}123^\circ$ under 8 mm. pressure.

Phenylmethylcarbinol and phenylethylcarbinol have been prepared by the action of benzaldehyde on magnesium methiodide and magnesium ethobromide respectively. Phenylpropylcarbinol, $\text{CHPr}^a\cdot\text{Ph}\cdot\text{OH}$, from benzaldehyde and magnesium propylbromide, boils at $113\text{--}115^\circ$ under 10 mm. pressure, has the sp. gr. 0.997 at 0° , 0.9861 at $13.7^\circ/4^\circ$, and n_D 1.51914 at 13.7° . The acetate boils at $117\text{--}118^\circ$ under 8 mm. pressure. Phenylisopropylcarbinol, from benzaldehyde and magnesium isopropylbromide, boils at $112\text{--}113^\circ$ under 15 mm. pressure, has the sp. gr. 0.9986 at 0° , 0.9869 at $13.7^\circ/4^\circ$, and n_D 1.51932 at 13.7° . The acetate boils at $122\text{--}125^\circ$ under 20 mm. pressure. Phenylisobutylcarbinol has the sp. gr. 0.9726 at 0° , 0.9597 at $17.6^\circ/4^\circ$ and n_D 1.50798 at 17.6° . The acetate boils at $125\text{--}126^\circ$ under 9 mm. pressure. Phenylisoamylcarbinol, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}_2$, from

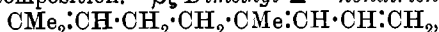
benzaldehyde and magnesium *isoamyl*bromide, boils at 132° under 8 mm. pressure, has the sp. gr. 0.9674 at 0° , 0.9536 at $18.5^{\circ}/4^{\circ}$ and n_D 1.50714 at 18.5° . The *acetate*, boils at $137-139^{\circ}$ under 9 mm. pressure. *2-Furfurylisoamylcarbinol*, $C_4OH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot Pr^{\beta}$, from furfuraldehyde and magnesium *isoamyl*bromide, has a faint odour which does not resemble that of furfuraldehyde, boils at 110° under 8 mm., at 118° under 14 mm. pressure, has the sp. gr. 0.9998 at 0° , 0.9882 at $12^{\circ}/4^{\circ}$, and n_D 1.47939 at 12° . The *acetate* has a penetrating odour and quickly becomes yellow; it boils at $123-124^{\circ}$ under 14 mm. pressure. By the action of magnesium benzylbromide on aldehydes, only dibenzyl is formed.

By the action of acetone on magnesium methiodide and magnesium *tert.*butyl iodide, respectively, trimethylcarbinol and pentamethylethanol, $CMe_3 \cdot CMe_2 \cdot OH$, are obtained, the last, however, only in very small quantity and in the form of the hydrate. Dimethyl*isoamyl*carbinol, $OH \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot Pr^{\beta}$, from acetone and magnesium *isoamyl*bromide, boils at $150-153^{\circ}$ under 756 mm. pressure, has the sp. gr. 0.8203 at 0° , 0.8115 at $11.4^{\circ}/4^{\circ}$, and n_D 1.42428 at 11.4° . The *acetate* has an odour like that of cedar wood, and boils at $171-173^{\circ}$ under 745 mm. pressure. Phenyl*dimethyl*carbinol crystallises in small prisms, melts at 23° , and boils at 91° under 8 mm. pressure. Benzyl*dimethyl*carbinol melts at 0° , has the sp. gr. 0.9960 at 0° , 0.9822 at $13.7^{\circ}/4^{\circ}$, and n_D 1.51950 at 13.7° . α -Naphthyl*dimethyl*carbinol boils at $159-161^{\circ}$ under 9 mm. pressure and is easily soluble in ether, methyl alcohol, alcohol, benzene, or ethyl acetate, and slightly so in light petroleum.

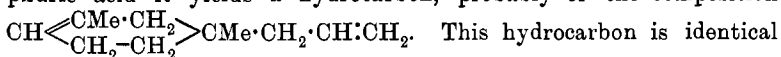
By the action of organomagnesium compounds on the esters of monobasic acids, tertiary alcohols are formed except in the cases of the esters of formic acid which yield secondary alcohols. Diethylcarbinol, $CHEt_2 \cdot OH$, from ethyl formate and magnesium ethylbromide, boils at $114-115^{\circ}$ under 749 mm. pressure, has the sp. gr. 0.8391 at 0° , 0.8271 at $14.7^{\circ}/4^{\circ}$, and n_D 1.41243. Di*isoamyl*carbinol has the sp. gr. 0.840 at 0° , 0.8305 at $12.6^{\circ}/4^{\circ}$, and n_D 1.43801 at 12.6° . Methyl*diisoamyl*carbinol has the sp. gr. 0.847 at 0° , 0.8373 at $12.3^{\circ}/4^{\circ}$, and n_D 1.44253. The *acetate* boils at 120° under 16 mm. pressure, has the sp. gr. 0.864 at $16.9^{\circ}/4^{\circ}$, and n_D 1.43191 at 16.9° . Phenyl*dimethyl*carbinol is formed by the action of magnesium methiodide on methyl benzoate.

In many of the preceding reactions, hydrocarbons are formed by the elimination of water from the alcohols and in some cases they constitute the main products. The following hydrocarbons have been prepared in this way or by the action of acetic anhydride on the corresponding alcohols. $\beta\delta$ -Dimethyl- Δ^{83} -pentadiene, has the sp. gr. 0.7595 at 0° , 0.7490 at $12^{\circ}/4^{\circ}$, and n_D 1.44684 at 12° . The *tetrabromide* is a stable liquid. The *dihydrobromide* boils at $83-84^{\circ}$ under 7 mm. pressure. By the action of an 80 per cent. solution of sulphuric acid on the hydrocarbon, it forms the dimeric compound, $(C_7H_{12})_2$, which boils at $98-100^{\circ}$ under 12 mm. pressure, has the sp. gr. 0.8869 at 0° , 0.8706 at $10^{\circ}/4^{\circ}$, and n_D 1.48483 at 10° . $\beta\zeta$ -Dimethyl- Δ^{85} -heptadiene, $CHMe_2 \cdot CH_2 \cdot CH \cdot CH \cdot CMe \cdot CH_2$, from synthetical methylheptenone and magnesium methiodide, boils at $143-145^{\circ}$ under 755 mm. pressure, has a sp. gr. 0.7648 at $10^{\circ}/4^{\circ}$, and n_D 1.46202 at 10° . The *dihydrobromide* boils at $110-112^{\circ}$ under 10 mm. pressure

with slight decomposition. $\beta\zeta$ -Dimethyl- Δ^{85} -nonatriene,



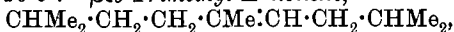
from citral and magnesium methiodide, has a pleasant odour of lemons, boils and decomposes at $195-197^\circ$ under 750 mm., and boils at $76-78^\circ$ under 8 mm. pressure; it has the sp. gr. 0.8215 at 0° , 0.814 at $11.3^\circ/4^\circ$ and n_D 1.48686 at 11.3° . By the action of hydrogen bromide, it forms two or more isomeric trihydrobromides which are partly solid and partly liquid and when treated with an 80 per cent. solution of sulphuric acid it yields a hydrocarbon, probably of the composition



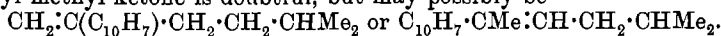
This hydrocarbon is identical with that prepared from homolinalool by Tiemann (Abstr., 1896, i, 271); it has an odour like that of terpene, boils at $67-69^\circ$ under 9 mm., and at $183-185^\circ$ under 741 mm. pressure, has the sp. gr. 0.8525 at 0° , 0.8450 at $9.9^\circ/4^\circ$, and n_D 1.47281 at 9.9° . The *dihydrobromide* boils at $130-135^\circ$ under 10 mm. pressure.

The *terpene*, $\text{CMe} \begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{CH}_2) \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{C} \cdot \text{CMe}_2$, from pulegone and magnesium methiodide, has a terpene-like odour, boils at $64-65^\circ$ under 9 mm., and at $177-179^\circ$ under 744 mm. pressure, has the sp. gr. 0.8518 at 0° , 0.8479 at $8.9^\circ/4^\circ$, and n_D 1.47860 at 8.9° . By the action of bromine, it forms a mixture of dibromide and tetrabromide; the *hydrobromide* is a liquid. 3-Methenementhane, $\text{CHMe} \begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{CH}_2) \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{CH} \cdot \text{CHMe}_2$,

from menthone and magnesium methiodide, boils at $72-74^\circ$ under 10 mm. pressure, has the sp. gr. 0.8452 at 0° , 0.8371 at $10.6^\circ/4^\circ$, and n_D 1.46510 at 10.6° . $\beta\epsilon\theta$ -Trimethyl- Δ^6 -nonene,



from methyl-diisocamylcarbinol, acetic anhydride, and sodium acetate, boils at $74-76^\circ$ under 9 mm. pressure, has the sp. gr. 0.7768 at 0° , 0.7678 at $12.3^\circ/4^\circ$, and n_D 1.43521 at 12.3° . Phenylmethylethylene, $\text{CMePh} \cdot \text{CH}_2$, prepared by the action of acetic anhydride on phenyl-dimethylcarbinol, boils at 106° under 126 mm., and at $158-160^\circ$ under 748 mm. pressure, has a sp. gr. 0.9165 at $9.6^\circ/4^\circ$, and n_D 1.54207 at 9.6° . The *dibromide* boils and decomposes at $111-114^\circ$ under 7 mm. pressure. When the hydrocarbon is heated with concentrated hydrochloric acid under pressure, it polymerises, forming the *hydrocarbon* $\text{C}_{18}\text{H}_{20}$, which crystallises in triclinic prisms, melts at $52-53^\circ$, and boils at $158-159^\circ$ under 8 mm. pressure. α -Phenyl- β -methyl- Δ^6 -propylene, $\text{CHPh} \cdot \text{CMe}_2$, prepared from benzyl-dimethylcarbinol, boils at $76-77^\circ$ under 11 mm., and at $183-185^\circ$ under 748 mm. pressure, has a sp. gr. 0.9298 at 0° , and yields a liquid *dibromide*. α -Phenyl- γ -methyl- Δ^4 -tetradiene, $\text{CHPh} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CH}_2$, prepared by the action of acetic anhydride on the product obtained from benzylideneacetone and magnesium methiodide, forms crystals, melts at 27° , boils at 115° under 18 mm. pressure, and polymerises readily. The composition of the hydrocarbon formed by the action of magnesium *iso*amylbromide on β -naphthyl methyl ketone is doubtful, but may possibly be

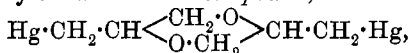


The organomagnesium compounds are more generally applicable, more convenient to handle, and give better yields in the synthesis of

monobasic acids, alcohols, and hydrocarbons than the organozinc compounds.
E. W. W.

Cyclic Mercury-Carbon Compounds. By JULIUS SAND (*Ber.*, 1901, **34**, 2910—2915).—When ethyl ether mercuric bromide (*Abstr.*, 1900, i, 618) is reduced with alkaline stannite solution, it yields *mercuriodiethylene oxide*, $\text{O}:(\text{C}_2\text{H}_4)_2:\text{Hg}_2$, in the form of a bluish-black precipitate which sinters at 80° and melts between 140° and 150° ; it is insoluble in water, alkalis, and the usual organic solvents, is completely decomposed by hot hydrochloric acid, and when heated with benzene at 140° is converted into mercury and *mercuriodiethylene oxide*, $\text{O} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{Hg}$; this crystallises in glistening, colourless needles with a characteristic odour, melts at 145° , and is insoluble in water, alkalis, and dilute mineral acids, but is readily soluble in most organic solvents with the exception of ether and acetone. It is not decomposed when heated with potassium hydroxide, iodide, or cyanide; but with fuming hydrochloric acid gives a theoretical yield of ethylene. It forms a *mercurichloride*, $\text{C}_4\text{H}_8\text{OHg} \cdot 2\text{HgCl}_2$, and also a complex *picrate* decomposing at 80° .

Dipropylene oxide mercuric bromide (this vol., i, 458) and alkaline stannite solution yield a brick-red compound,



which turns brown on exposure to light, and after ten hours' exposure and subsequent extraction with benzene, yields a *mercuri-compound*, $\text{C}_8\text{H}_{10}\text{O}_2\text{Hg}$, which melts at about 190° , is insoluble in water, alkalis, dilute acids, or acetone, but readily soluble in benzene or toluene, is decomposed by concentrated hydrochloric acid, and gives precipitates with mercuric chloride and picric acid.
J. J. S.

Acetylacetone Compounds of Platinum. By ALFRED WERNER (*Ber.*, 1901, **34**, 2584—2593).—When potassium platinumchloride, K_2PtCl_4 , is heated with about 10 times its weight of 10 per cent. aqueous potassium hydroxide until the liquid has acquired a yellowish shade, shaken with twice its weight of acetylacetone, and the heating and shaking continued for a time, a bright yellow, crystalline powder separates. By further treatment with a little strong potash and acetylacetone, the mother liquor can be made to yield more crystals; this treatment can be repeated several times. The substance in question is *platinum acetylacetonate*, PtA_2 , where A is $\cdot\text{O} \cdot \text{CMe} : \text{CH} : \text{CMe} \cdot \text{O}$ or $\cdot\text{CH}(\text{CMeO})_2$, according as the substance is regarded as derived from the enolic or the ketonic form of acetylacetone. It is not decomposed by strong mineral acids, and does not give a coloration with ferric chloride. It raises the boiling point of chloroform by an amount corresponding with that required by the formula given.

When a 25 per cent. solution of potassium platinumchloride is heated to boiling, shaken with half its weight of acetylacetone and one-fourth its weight of 25 per cent. aqueous potassium hydroxide, and shaken again after 10 minutes with as much more potash, orange-yellow crystals

separate, followed after a time by bright yellow crystals. The first *salt*, $\text{KCl}, \text{PtCl}_4$, gives no red coloration with ferric chloride, or precipitate with salts of heavy metals; from its solution in water it can be salted out by potassium chloride or potassium hydroxide, but it is not precipitated by hydrochloric acid. The second *salt*, KA, PtCl_4 , gives a brownish-red coloration with ferric chloride in dilute solution, and a brown precipitate in strong solution; it gives precipitates also with the salts of other heavy metals. When shaken with methyl sulphate and aqueous potassium hydroxide, it yields an oil which crystallises eventually, and is presumably a methyl derivative. When its aqueous solution is mixed with hydrochloric acid, a yellow, amorphous *substance*, HA, PtCl_4 , is precipitated. This is soluble in organic solvents; alkalis also dissolve it, and it is reprecipitated in the crystalline form from these solutions by hydrochloric acid. When freshly precipitated, it dissolves in water, but is reprecipitated from this solution by hydrochloric acid. After it has been kept, it dissolves to a smaller extent in water, but the solution is no longer precipitated by hydrochloric acid; probably a transformation of the HA group from the enolic to the ketonic form has taken place. When a solution of it in ammonia is mixed with rubidium chloride, a yellow, crystalline *salt*, $\text{RbA}, \text{PtCl}_4$, is precipitated.

When a hot 25 per cent. solution of potassium platinochloride is mixed with about half its weight of acetylacetone and half its weight of 33 per cent. aqueous sodium hydroxide, a golden-yellow *salt*, $\text{NaCl}, \text{PtCl}_4, \text{NaA}, 5\text{H}_2\text{O}$, is precipitated; this gives at once a deep red coloration with ferric chloride, and precipitates with the salts of heavy metals. When a strong aqueous solution of it is boiled until the colour has become dark, but not quite black, and then saturated with sodium chloride, a yellow *salt* is precipitated which can be crystallised from chloroform; it is then greenish-yellow in colour, and has the composition $\text{NaA}, \text{PtCl}_4, 2\text{H}_2\text{O}, \text{CHCl}_3$. This salt is a derivative of the substance, HA, PtCl_4 , described above, for this substance is precipitated when a solution of the salt is mixed with hydrochloric acid.

C. F. B.

Hexamethylene [*cycloHexane*]. By NICOLAI D. ZELINSKY (*Ber.*, 1901, 34, 2799—2803. Compare *Abstr.*, 1895, i, 411).—*cycloHexane*, prepared by Baeyer's method, melts at 2° , boils at $80.8\text{--}81^\circ$ (corr.), has a sp. gr. 0.7763 at $20^\circ/4^\circ$, and the refractive index n_D 1.4269 at 18° (compare *loc. cit.*). The crystals belong to the regular system and act very feebly on polarised light. *cycloHexanone*, prepared from pimelic acid, boils at 155.4° (corr.), and has a sp. gr. 0.9467 at $19^\circ/4^\circ$ and n_D 1.4503 at 19° . The *cyclohexanol*, obtained from the ketone, boils at 160.9° (corr.), has a sp. gr. 0.9471 at $22^\circ/4^\circ$, and n_D 1.4650 at 22° .

In the reduction of *cyclohexanone* with sodium, *cyclohexanol* is formed together with *cyclohexanepinacone*, $\text{C}_{12}\text{H}_{22}\text{O}_2$, which crystallises in small, white needles melting at $129\text{--}130^\circ$.

When *cyclohexane* is prepared by reduction of *cyclohexanyl iodide* by zinc dust in the presence of dilute alcohol (compare *Abstr.*, 1899, i, 181), it melts at 6.4° , boils at $80.8\text{--}80.9^\circ$ (corr.), has a sp. gr. 0.7788 at $19.5^\circ/4^\circ$, and n_D 1.4266 at 19.5° . These constants closely approxi-

mate to those found for *cyclohexane* obtained by Young and Fortey (*Trans.*, 1899, 75, 880) from naphtha, and for hexamethylene, prepared by Sabatier and Senderens (this vol., i, 263, 459) by reduction of benzene.

On heating *cyclohexane* under pressure with excess of bromine at 150—200° for several days, 1:2:4:5-tetrabromobenzene (m. p. 177—178°) is formed. K. J. P. O.

Oxidation of Homologues of Benzene. By EYVIND BOEDTKER (*Bull. Soc. Chim.*, 1901, [iii], 25, 843—852).—The oxidation of cumene (*isopropylbenzene*) by chromic acid in acetic acid solution gives rise to the formation of about 10 per cent. of *phenyldimethylcarbinol*, $\text{CMe}_2\text{Ph}\cdot\text{OH}$, a colourless, highly refracting liquid of strong aromatic odour, which boils and partially decomposes at 215—220°, does not solidify at -18° , has a sp. gr. 1.0177 at 20°, and n_D 1.5314 at 18.5°.

According to Mensel, cumene, when treated with bromine, yields *o*-bromocumene and a solid substance which is now shown to be a hydrocarbon, $\text{C}_{17}\text{H}_{14}$, to which the name 3:5-diphenylisocyclopentenine

and the constitution $\text{CH} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH} \\ \diagdown \quad \diagup \\ \text{CH} \end{array} \text{CH}$ are assigned; it crystallises in

white scales melting at 211° (corr.), distils above 300°, is not acted on by the halogens or by chromic acid, and is insoluble in alcohol but more or less soluble in other organic solvents.

The oxidation of toluene by chromic acid in acetic acid solution leads to the production of benzyl alcohol, benzyl acetate, dibenzyl, and other compounds which were not identified. N. L.

Replacement of Oxygen by Fluorine in the Iodoxy-compounds. By RUDOLPH F. WEINLAND and W. STILLE (*Ber.*, 1901, 34, 2631—2633. Compare *Abstr.*, 1899, ii, 363).—Iodoxy-compounds are converted by concentrated hydrofluoric acid into iodosofluorides, one atom of oxygen being displaced by two atoms of fluorine. The crystals are stable in dry air, but are decomposed by moist air and by water. When heated, they decompose explosively. *Benzene iodosofluoride*, IPhOF_2 , crystallises in lustrous, matted needles and decomposes at 216°. *o*-Tolueneiodosofluoride, $\text{C}_6\text{H}_4\text{Me}\cdot\text{IOF}_2$, crystallises in leafy aggregates of granules; it commences to melt at 120°, and decomposes at 170—190°. *p*-Tolueneiodosofluoride, crystallises in lustrous needles and decomposes at 206°. A. H.

Electrolytic Reduction of Nitro-compounds to Amines. C. F. BOEHRINGER & SONS (D.R.-P. 117007).—Nitrobenzene (4 parts) mixed in the cathode cell with 16 parts of concentrated hydrochloric acid diluted with its own weight of water, is quantitatively converted into aniline, when cuprous chloride (1 part) is added, and the reduction carried out by an electric current, having a density of 1900 amperes per sq. m., the electrodes being of platinum or other refractory material, and the anode cell containing 10 per cent. sulphuric acid. Similar results are obtained by adding iron, chromium, lead, and mercury salts, or the corresponding metals in a finely divided con-

dition. (Compare D.R.-P. 116942, and this vol., i, 587). Finely divided tin or a tin salt may be placed in the anode cell (Eng. Pat. 4175 of 1900).
G. T. M.

Electrolytic Oxidation of Nitrotoluenes. By P. PIERRON (*Bull. Soc. Chim.*, 1901, [iii], 25, 852—854).—It has been shown by Elbs (Abstr., 1897, i, 332) that *p*-nitrotoluene yields *p*-nitrobenzyl alcohol when oxidised electrolytically, and it is now shown that *o*- and *m*-nitrotoluene, when similarly treated, yield principally *o*-nitrobenzyl alcohol and *m*-nitrobenzaldehyde respectively. The nitrotoluene is dissolved in a mixture of acetic and sulphuric acids and the liquid electrolysed at 90° between a platinum anode and a nickel cathode, using a current of 1 ampere.
N. L.

Phenyldinitromethane [ω -Dinitrotoluene]. By GIACOMO PONZIO (*Gazzetta*, 1901, 31, ii, 133—138).—The author has succeeded in preparing this compound by starting from benzyl methyl ketone, which, by the action of sodium ethoxide and amyl nitrite, is converted into isonitrosobenzyl methyl ketone; to the latter compound, suspended in anhydrous ether cooled in ice, the calculated quantity of nitrogen peroxide, previously distilled over phosphoric oxide, is then added. ω -Dinitrotoluene, $\text{C}_6\text{H}_5(\text{NO}_2)_2$, crystallises from ether in large, white prisms melting at 79°. It is soluble in the cold, in organic solvents with the exception of light petroleum, and in hot water, and, with the formation of a yellow coloration, in alkali solutions, but resists the action of dilute acids. It is volatile in a current of steam and gives the normal molecular weight in boiling ether or freezing acetic acid. When heated above 130°, it is decomposed violently, yielding red vapours and benzaldehyde. It dissolves without apparent change in concentrated sulphuric acid, but on heating the solution red vapours are evolved and benzoic acid formed. With phenol and sulphuric acid, it gives no coloration in the cold, but on heating gently the liquid assumes an intense emerald green colour which changes to red on adding water. When reduced, either with glacial acetic acid and zinc dust at a low temperature, or with stannous chloride, it yields benzaldehyde. It does not react with acetic anhydride, acetyl chloride, or phosphorus tri- or penta-chloride. The *potassium* derivative, $\text{C}_6\text{H}_5\text{K}(\text{NO}_2)_2$, obtained by the action of alcoholic potassium hydroxide, is precipitated in the form of sparkling, yellow laminae which are very soluble in water and slightly so in alcohol and when heated explode; when reduced with sodium amalgam or with stannous chloride in presence of sodium carbonate and potassium sodium tartrate, it yields benzaldehyde and ammonia. The *silver* salt, $\text{C}_6\text{H}_5\text{Ag}(\text{NO}_2)_2$, crystallises from water in brownish-yellow prisms which explode when heated.
T. H. P.

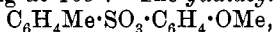
Action of Nitric Acid on *o*-Nitrotoluene-*p* sulphonamide.
Nitration of *p*-Toluenesulphonic Chloride. By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEU (*Ber.*, 1901, 34, 2992—2996).—*o*-Nitrotoluene-*p*-sulphonamide, when treated with fuming nitric acid, gives rise to two mononitrotoluenesulphonic acids and a dinitrotoluenesulphonic acid;

the acid seems to have a hydrolytic action, adding the elements of water to the sulphonamide with the formation of an ammonium salt; the production of isomeric mononitro-derivatives points to a simultaneous wandering of the nitro-group.

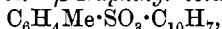
o-Nitrotoluene-*p*-sulphonic acid is isolated from the products of nitration in the form of its *aniline* and *ammonium* salts, these compounds crystallising from water or alcohol in colourless needles melting respectively at 225° and 221°. The isomeric *ammonium nitrotoluenesulphonate*, obtained from the mother liquors of the preceding ammonium compound, melts at 290°. *Ammonium dinitrotoluenesulphonate* is a white, crystalline substance which does not melt below 300°. *p*-Toluenesulphonic chloride, when nitrated on the water-bath with a mixture of fuming nitric acid and concentrated sulphuric acid, yields 2 : 6-dinitrotoluene-4-sulphonic acid in almost theoretical yield.

G. T. M.

Derivatives of Toluene-*p*-sulphonic Chloride and *o*-Nitrotoluene-*p*-sulphonic Chloride. By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1901, 34, 2996—3004).—Toluene-*p*-sulphonic chloride and its nitro-derivative, when condensed with the phenols in the presence of sodium carbonate, readily yield esters of toluene-*p* sulphonic acid. The *o*-nitrophenyl ester, $C_6H_4Me \cdot SO_3 \cdot C_6H_4 \cdot NO_2$, forms colourless crystals melting at 98°; *o*-nitrophenyl *o*-nitrotoluene-*p*-sulphonate, $NO_2 \cdot C_6H_4Me \cdot SO_3 \cdot C_6H_4 \cdot NO_2$, crystallises in colourless needles and melts at 113—114°. These compounds, when reduced, yield bases which, on diazotising and combining with α -naphthol-4-sulphonic acid, give rise to red azo-colouring matters. The *resorcinol* esters, $C_6H_4(SO_3 \cdot C_6H_4Me)_2$ and $C_6H_4(SO_3 \cdot C_6H_3Me \cdot NO_2)_2$, crystallise in prisms melting respectively at 80—81° and 136°. The latter compound on nitration yields a *mononitro* derivative crystallising in colourless needles and melting at 105°. The *guaiacyl* ester,

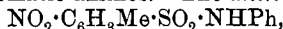


melts at 85° and is readily hydrolysed by concentrated acids or alcoholic potassium hydroxide; it forms a *nitro*-derivative, $C_6H_4Me \cdot SO_3 \cdot C_6H_3(NO_2) \cdot OMe$, crystallising in prisms and melting at 145°; the product, when hydrolysed with concentrated sulphuric acid yields 4-nitro-1 : 2-guaiacol. *β -Naphthyl toluene-*p*-sulphonate*,



crystallises in nacreous leaflets, and melts at 125°; the corresponding ester, $C_{10}H_6(SO_3 \cdot C_6H_4Me)_2$, from 2 : 7-dihydroxynaphthalene, melts at 150° and is insoluble in alkaline solutions.

The two sulphonic chlorides readily yield substituted amides when condensed with the aromatic amines. The *anilide*,



melts at 109°; *toluenesulphone-2 : 4-dinitroanilide*,

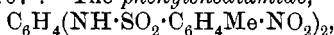


produced on nitrating the anilide, melts at 219°; the *nitro*-compound, $NO_2 \cdot C_6H_3Me \cdot SO_2 \cdot NH \cdot C_6H_3(NO_2)_2$, obtained in a similar manner from the corresponding anilide, melts at 214°.

The *phenylhydrazide*, $NO_2 \cdot C_6H_3Me \cdot SO_2 \cdot NH \cdot NHPh$, melts at

157—158°; it yields an amine on reduction, the diazonium salt of which furnishes an azo-compound with α -naphthol-4-sulphonic acid.

The *phenetidine*, $C_6H_4Me \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot OEt$, crystallises in needles and melts at 106—107°. The *phenylenediamide*,



obtained from *m*-phenylenediamine, melts above 300° and yields on reduction an amine which gives rise to red azo-compounds.

Bis toluene-p-sulphone-p-phenylenediamide, $C_6H_4(NH \cdot SO_2 \cdot C_6H_4Me)_2$, melts above 250°.

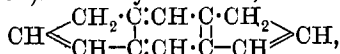
The *naphthalides*, $NO_2 \cdot C_6H_3Me \cdot SO_2 \cdot NH \cdot C_{10}H_7$, derived from α - and β -naphthylamine, melt at 157° and 161° respectively, and yield on reduction amines forming well crystallised hydrochlorides and giving rise to red azo-colouring matters. G. T. M.

1:5-Chloronitronaphthalene from 1-Chloronaphthalene. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D. R.-P. 120585).—The crude product from the nitration of 1-chloronaphthalene, when treated with alcoholic ammonia at 170—180°, yields a mixture of 4-nitro- α -naphthylamine and unaltered 1:5- and 1:8-chloronitronaphthalenes. The chloronitronaphthalenes are removed by extraction with carbon tetrachloride or a mixture of carbon disulphide and light petroleum, and the residue left after distilling off the solvent is crystallised from alcohol in order to free the 1:5-compound from traces of the 1:8-isomeride. G. T. M.

Preparation of 1:5-Dinitro- and 1:3:8-Trinitro naphthalenes. KALLE & Co. (D. R.-P. 117368).—Nitronaphthalene dissolved in 6 parts of concentrated sulphuric acid, and nitrated with concentrated nitric acid (1 mol.), mixed with 2.5 parts of concentrated sulphuric acid, yields a product from which 1:5-dinitronaphthalene (m. p. 211°) separates on cooling; the mother liquor, on further nitration, yields 1:3:8-trinitronaphthalene (m. p. 218°). The 1:8-dinitro-compound partly separates along with its isomeride when a smaller quantity of sulphuric acid is employed. G. T. M.

Preparation of Dinitronaphthalenesulphonic Acids. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D. R.-P. 117268).—Although 1:5- and 1:8-dinitronaphthalenes are converted by excess of fuming sulphuric acid into nitrosonitronaphthols (Graebe, Abstr., 1900, i, 24; Friedländer, *ibid.*, 150), yet, when treated with acid containing very little sulphur trioxide, they yield dinitronaphthalenesulphonic acids. The dinitro-compound, dissolved in 6 parts of ordinary concentrated sulphuric acid, is treated with 2 parts of 20 per cent. fuming acid slowly added, the mixture is then poured into brine solution, when the sodium salt of the monosulphonic acid separates, and may be crystallised from alcohol. The 1:5-compound yields 1:5-dinitronaphthalene-3-sulphonic acid, of which the *chloride* melts at 118—119°; the 1:8-isomeride gives rise to 1:8-dinitronaphthalene-3-sulphonic acid, of which the *chloride* melts at 143—144° (compare D. R.-P. 85058). G. T. M.

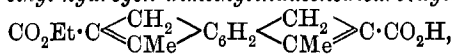
Synthesis of Indacene Derivatives. By FRITZ EPHRAIM (*Ber.*, 1901, 34, 2779—2794).—The hydrocarbon,



is termed indacene, and its tetrahydro-derivative, $\text{C}_{12}\text{H}_{14}$, hydrindacene. The author has obtained derivatives of indacene and of tetraketohydrindacene by the condensation of ethyl *m*-xylylenediaceoacetate and of ethyl benzene-1:2:4:5-tetracarboxylate with ethyl acetate (compare Wislicenus and Kötze, *Abstr.*, 1889, 1067, 1068).

The sodium salt of ethyl tetraketohydrindacenedicarboxylate, $\text{CO}_2\text{Et} \cdot \text{CNa} \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_2 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CNa} \cdot \text{CO}_2\text{Et}$, is a brick-red powder, and is prepared by adding ethyl acetate slowly to ethyl benzene-1:2:4:5-tetracarboxylate and sodium heated at 100° ; the free ester is a red powder.

Ethyl *m*-xylylenediaceoacetate, $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{CHAc} \cdot \text{CO}_2\text{Et})_2$, prepared from ω -dibromo-*m*-xylene, ethyl acetoacetate, and sodium ethoxide, is a colourless, viscous oil. On treating the ester with 80 per cent. sulphuric acid, ethyl hydrogen dimethylindacenedicarboxylate,



is formed, and crystallises from water in colourless, microscopic needles melting at 165 – 166° ; the silver salt forms white flakes. Dimethylindacenedicarboxylic acid, prepared by hydrolysing the ester by potassium hydroxide, is a brownish-yellow powder melting above 300° . The tetrabromide, dimethyltetrabromohydrindacenedicarboxylic acid, $\text{C}_{16}\text{H}_{14}\text{O}_4\text{Br}_4$, is prepared by the action of bromine on the acid or its monoethyl ester, and is a white, crystalline powder, which does not melt at 300° .

Dimethylindacene, $\text{C}_6\text{H}_2(\begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{CMe} \diagup \end{array} \text{CH})_2$, obtained by distilling dimethylindacenedicarboxylic acid with soda-lime, is a yellowish oil, boiling without decomposition at a high temperature, and has a characteristic odour resembling that of indene; when exposed to the air, it resinifies.

When distilled under reduced pressure or when kept, ethyl *m*-xylylenediaceoacetate is converted into a syrup, which, on treatment with 80 per cent. sulphuric acid, yields a neutral substance, $\text{C}_{18}\text{H}_{18}\text{O}_4$; with bromine, this gives a dibromide.

Many fruitless attempts were made to prepare indacene derivatives from *p*-phenylenediacyrylic and *p*-phenylenedipropionic acids. *p*-Phenylenediacyrylic acid can be directly prepared from terephthalaldehyde by Perkin's reaction (compare Löw, *Abstr.*, 1886, 461). Methyl-*p*-aldehydocinnamate, $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{Me}$, prepared from *p*-aldehydocinnamic acid, crystallises in white needles melting at 82 – 83° . *p*-Phenylenetetrabromodipropionic acid, prepared from *p*-phenylenediacyrylic acid and bromine, is a white, crystalline powder melting at 251° (compare Löw, *loc. cit.*); its sodium salt decomposes in solution, with the formation of *p*-phenylenedibromodiethylene, $\text{C}_6\text{H}_4(\text{CH} \cdot \text{CHBr})_2$, which crystallises in needles melting at 135° .

p-Xylylenedichloromalonic acid, $C_6H_4[CH_2 \cdot CCl(CO_2H)]_2$, prepared from the corresponding ethyl ester, forms crystals which melt and decompose at 179° ; the potassium salt crystallises in needles. On heating the acid alone or with concentrated sulphuric acid, *p*-phenylenedichloropropionic acid, $C_6H_4(CH_2 \cdot CHCl \cdot CO_2H)_2$, is obtained, and forms crystals melting at 165° .

Ethyl *p*-xylylenedimethylmalonate, $C_6H_4[CH_2 \cdot CMe(CO_2Et)]_2$, prepared from the sodium salt of ethyl *p*-xylylenedimalonate and methyl iodide, crystallises in groups of needles melting at 75° ; on hydrolysis of the ester with potassium hydroxide, the potassium salt was obtained as long, white needles. From the latter an oily acid (probably *p*-xylylenedimethylmalonic acid) was prepared, which, when heated with water under pressure finally at 175° , yielded *p*-phenylenediisobutyric acid, $C_6H_4(CH_2 \cdot CHMe \cdot CO_2H)_2$; this acid forms small, white crystals melting at 169° .
K. J. P. O.

Condensation Products of 2:4-Dinitrotoluene. By JOHANNES THIELE and RICHARD ESCALES (*Ber.*, 1901, 34, 2842—2848).—Dinitrotoluene condenses with benzaldehyde in the presence of piperidine, forming stilbene derivatives. The piperidine can be replaced by other amines, such as diethylamine, triethylamine, or ammonia, but the yields are much smaller. 2:4-Dinitrostilbene, $C_{14}H_{10}O_4N_2$, separates from acetic acid in bright yellow, compact crystals melting at 139 — 140° , and forms a dibromide, $C_{14}H_{10}O_4N_2Br_2$, which crystallises from xylene in white prisms melting and decomposing at 185 — 186° . When reduced with stannous chloride and hydrochloric acid in glacial acetic acid solution, it yields 2:4-diaminostilbene, $C_{14}H_{14}N_2$, which crystallises from benzene in bright yellow, lustrous needles melting at 119 — 120° , and forms a dihydrochloride, which crystallises, with $2H_2O$, in needles.

When 2:4 dinitrostilbene is partially reduced under the conditions just described, the compound obtained is probably 4-nitro-2-aminostilbene, $C_{14}H_{12}O_2N_2$; this separates from alcohol in reddish crystals, melts at 142 — 143° , and yields a hydrochloride which melts at 218 — 219° and is decomposed by water, and an acetyl derivative, $C_{16}H_{14}O_3N_2$, which crystallises in bright yellow, felted needles and melts at 220° . The partial reduction of 2:4-dinitrostilbene with ammonium sulphide yields a compound which is probably 2-nitro-4-aminostilbene; this separates from alcohol in ruby-coloured crystals, melts at 110 — 111° , and forms a hydrochloride which crystallises in golden laminæ melting at 223° , and an acetyl derivative which crystallises in flat, orange coloured plates and melts at 192 — 193° .

2:4:4'-Trinitrostilbene, $C_{14}H_9O_6N_3$, obtained when *p*-nitrobenzaldehyde is used in the condensation, crystallises from nitrobenzene in lemon-coloured, felted needles and melts at 240° . When reduced with stannous chloride, it yields 2:4:4'-triaminostilbene, $C_{14}H_{15}N_3$, which crystallises from toluene in small, yellow clumps and melts at 176 — 177° .

2:4:3'-Trinitrostilbene, obtained from *m* nitrobenzaldehyde, crystallises from acetic acid in yellow, felted needles, melts at 183 — 184° , and, when reduced, yields 2:4:3'-triaminostilbene, which forms small, yellow crystals melting at 112 — 113° .

2:4:2'-Trinitrostilbene separates from acetic acid in greenish-yellow

crystals, melts at 194—195°, and, when reduced, yields 2:4:2'-*tri-aminostilbene*, which is obtained in lustrous, yellow crystals melting at 156—157°.

R. H. P.

Isomeric Diamino-bases of α -Cyanostilbene. By MARTIN FREUND (*Ber.*, 1901, **34**, 3104—3108).—4:4'-*Dinitro- α -cyanostilbene*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{CN}) \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, obtained by the nitration of α -cyano-stilbene or by the condensation of *p*-nitrobenzyl cyanide and *p*-nitrobenzaldehyde, crystallises in silky, yellow needles, melts at 215°, and when reduced with tin and hydrochloric acid yields the corresponding 4:4'-*diamino*-compound, which crystallises in small, reddish-brown needles and melts at 188°.

m-Nitrobenzyl cyanide condenses with *m*-nitrobenzaldehyde, forming 3:3'-*nitro- α -cyanostilbene*, which crystallises from glacial acetic acid, melts at 204°, and when reduced yields the corresponding *diamino*-base, which crystallises in yellow needles melting at 145—146°.

2:2'-*Nitro- α -cyanostilbene*, obtained by the condensation of the corresponding *o*-compounds, crystallises from glacial acetic acid and melts at 169—171°.

4:3'-*Diamino- α -cyanostilbene* crystallises in needles and melts at 108—110°; the condensation of *p*-nitrobenzyl cyanide and *o*-nitrobenzaldehyde in the presence of sodium ethoxide yields 4:2'-*dinitro- α -cyanostilbene* and 2:4'-*dinitro- β -hydroxy- α -cyanodiphenylethane*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{CN}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, which crystallises from glacial acetic acid and melts at 135—138°; 4:2'-*dinitro- α -cyanostilbene*, when reduced with tin and hydrochloric acid, yields the *hydrochloride* of 2-amino-3-aminophenylquinoline, which crystallises, with $2\text{H}_2\text{O}$, in slender, grey needles decomposing at 250°.

R. H. P.

Action of Sulphur Monochloride on Anthracene. By EDUARD LIPPMANN and ISIDOR POLLAK (*Ber.*, 1901, **34**, 2767—2769).—On treating anthracene, suspended in petroleum, with a solution of sulphur monochloride, hydrogen chloride is evolved, the anthracene dissolves, and *anthracene dithiochloride*, $\text{C}_{14}\text{H}_6 \cdot \text{S}_2\text{Cl}$, is obtained. This forms a pale yellow, crystalline, insoluble powder melting at 212°; it is unchanged by boiling alcoholic potassium hydroxide, is oxidised by chromic acid to sulphuric and hydrochloric acids and anthraquinone, and is reduced by zinc and acetic acid to a substance with acid properties which still contains sulphur and chlorine.

On allowing the interaction of sulphur monochloride and anthracene to proceed until the evolution of hydrogen chloride ceases, β -dichloroanthracene (m. p. 209°) and sulphur are formed.

K. J. P. O.

Triphenylmethyl. By MOSES GOMBERG (*Ber.*, 1901, **34**, 2726—2733. Compare this vol., i, 77, 319, 638).—The hydrocarbon triphenylmethyl, CPh_3 , can be isolated in small, colourless crystals by the action of acetone on a concentrated solution of triphenylchloromethane in benzene, or in long, colourless crystals by the action of ethyl formate; it soon becomes yellow, reacts vigorously with iodine, absorbs oxygen readily, forming triphenylmethyl peroxide, and melts at 125—128°; two molecular-weight determinations in freezing naphthalene gave $M = 330$ and 372 (calc. 243). The crystalline hydrocarbon dissolved in benzene gives about 86 per cent. of the theoretical yield of

peroxide when exposed to air; the residue consists chiefly of an oil containing C, 84.20; H, 6.97; O, 8.83 per cent. T. M. L.

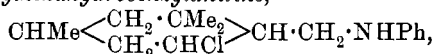
Action of Alcoholic Silver Nitrate on Aromatic Bases. By WILHELM VAUBEL (*Chem. Zeit.*, 1901, 25, 739—740. Compare Iachowicz, *Abstr.*, 1890, 445; Jørgensen, *ibid.*, 1886, 857; Hoogewerff and van Dorp, *ibid.*, 1881, 109; Mixter, *J. Amer. Chem. Soc.*, 1878, 1, 239).—When an alcoholic solution of silver nitrate is added to a similar solution of an aromatic base, a precipitate is produced consisting of a compound of 1 mol. of silver nitrate with 2 mols. of the base. Benzidine, tolidine, phenylacridine, β -naphthylamine, pyridine, and quinoline behave in this way. No compounds have been obtained with *p*-toluidine or indigotin. *o*-Toluidine gives a compound, the composition of which corresponds best with the formula $\text{AgNO}_3 \cdot 3\text{C}_7\text{H}_7 \cdot \text{NH}_2$. Aniline, acetanilide, and mono- and di-alkyl derivatives of aniline are more or less decomposed by alcoholic silver nitrate, the alkyl compounds yielding blue substances. J. J. S.

Tetrahydrobenzylamine Derivatives. FARBERWERKE VORM. MEISTER, LUCIUS, & BRUNING (D.R.-P. 119879).—The unsaturated base

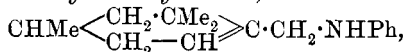
$\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{NHPh} \\ | \\ \text{CH} \end{smallmatrix}$ is obtained by converting the saturated hydroxylamine, $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{NHPh} \\ | \\ \text{CH} \cdot \text{OH} \end{smallmatrix}$ (compare following abstract), into

the *chloro*-base, $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{NHPh} \\ | \\ \text{CHCl} \end{smallmatrix}$, by the action of phosphorus pentachloride and hydrogen chloride in benzene solution, and subsequently heating the halogen derivative at 130° ; under these conditions, the substance undergoes rearrangement, and yields the hydrochloride of the new base. The free amine forms colourless crystals, melts at 38° , and boils at 211 — 213° under 20 mm. pressure.

Chlorotrimethylhexahydrobenzylamine,



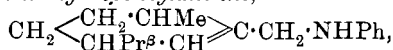
produced from hydroxytrimethylhexahydrobenzylamine by the action of phosphorus pentachloride and hydrogen chloride, is a yellow oil yielding *trimethyltetrahydrobenzylamine,*



when heated with an alcoholic solution of potassium hydroxide; the unsaturated base is a colourless oil boiling at 187° under 19 mm. pressure.

The *cis*- and *trans* hydroxymethylisopropylhexahydrobenzylamines yield *chloro*-bases which, by loss of hydrogen chloride, give rise to the same *methylisopropylhexahydrobenzylamine*; this is an oily base resembling coniine, and boils at 230° under the ordinary pressure.

Methylisopropyltetrahydrobenzylamine,



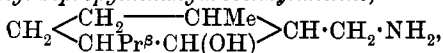
and *methylisopropyltetrahydrobenzylidimethylamine* are oils boiling respectively at 193° under 11 mm., and at 124 — 128° under 13 mm. pressure. G. T. M.

Hydroxyhexahydrobenzylamine Derivatives. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 119862).—Anilinomethylenecamphor (compare Abstr., 1895, i, 63), when reduced with sodium and ethyl alcohol, yields the base C_8H_{14} $\begin{matrix} \text{CH}\cdot\text{CH}_2\cdot\text{NHPh} \\ \text{CH}\cdot\text{OH} \end{matrix}$; this is a colourless syrup, which boils at 231° under 30 mm. pressure and yields a crystalline, sparingly soluble hydrochloride.

Hydroxymethylenedihydroisophorone, $\text{CHMe} \begin{matrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CH}_2-\text{CO} \end{matrix} \text{C}\cdot\text{CH}\cdot\text{OH}$, separates in the form of its sodium derivative when dihydroisophorone is heated with amyl formate and sodium ethoxide suspended in dry ether; the ketone set free by dilute acetic acid boils at 124° under 27 mm. pressure, and is a colourless oil having an odour resembling that of hydroxymethylenementhone. *Anilinomethylenedihydroisophorone*, $\text{CHMe} \begin{matrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CH}_2-\text{CO} \end{matrix} \text{C}\cdot\text{CH}\cdot\text{NHPh}$, produced by boiling the preceding compound with a solution of aniline in methyl alcohol and acetic acid, is a yellow, crystalline substance, which, on reduction with sodium and alcohol, yields *hydroxytrimethylhexahydrobenzylaniline*, $\text{CHMe} \begin{matrix} \text{CH}_2-\text{CMe}_2 \\ \text{CH}_2\cdot\text{CH}(\text{OH}) \end{matrix} \text{CH}\cdot\text{CH}_2\cdot\text{NHPh}$; this product crystallises from light petroleum in colourless needles, melts at $68-70^\circ$, and boils at 221° under 15 mm. pressure.

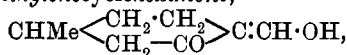
Aminomethylenementhone, $\text{CH}_2 \begin{matrix} \text{CH}_2\cdot\text{CHMe} \\ \text{CHPr}^s-\text{CO} \end{matrix} \text{C}\cdot\text{CH}\cdot\text{NH}_2$, crystallises from a solution of hydroxymethylenementhone in concentrated aqueous ammonia, and melts at 115° . *Hydroxymethylisopropylhexahydrobenzylamine*, $\text{CH}_2 \begin{matrix} \text{CH}_2-\text{CHMe} \\ \text{CHPr}^s\cdot\text{CH}(\text{OH}) \end{matrix} \text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$, obtained by reducing the preceding compound, is a colourless oil boiling at $150-152^\circ$ under 30 mm. pressure; it solidifies on cooling. The crude reduction product is a mixture of two stereoisomeric bases, which are separated by saturating its benzene solution with hydrogen chloride. The hydrochloride of the *trans*-base separates, whilst that of the *cis*-base remains dissolved. The two modifications solidify, after rectification, to a mass of white crystals; the *trans*-base boils at 163° , and the *cis*-base at $165-170^\circ$ under 30 mm. pressure.

Hydroxymethylisopropylhexahydrobenzylaniline,



prepared from anilinomethylenementhone, is an oil boiling at $247-248^\circ$ under 20 mm. pressure. *Hydroxymethylisopropylhexahydrobenzylidimethylamine* is obtained from dimethylaminomethylenementhone (an oily ketone forming a crystalline hydrate), and boils at 140° under 14 mm. pressure. *Hydroxymethylisopropylhexahydrobenzylethylamine* boils at $165-166^\circ$ under 19 mm. pressure.

Hydroxymethylmethylenecyclohexanone,



yields *anilinomethylmethylenecyclohexanone*, a yellow, crystalline ketone

melting at 170—171°, which, on reduction, yields *hydroxymethylhexahydrobenzylaniline*, $\text{CHMe} \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}(\text{OH}) \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{NHPh}$, a crystalline base melting at 126—127°. G. T. M.

Action of Aminosulphonic Acid on *p* Chloroaniline. By CARL PAAL (*Ber.*, 1901, **34**, 2748—2757. Compare *Abstr.*, 1894, i, 365; 1896, i, 235; 1897, i, 351).—The first product of the interaction of aminosulphonic acid and *p* chloroaniline is *p*-chloroaniline aminosulphonate; when heated above its melting point (160°), this salt decomposes with the production of ammonium *p*-chlorophenylaminosulphonate and *p*-chloroaniline *p*-chlorophenylaminosulphonate, together with ammonium sulphate and *p*-chloroaniline sulphate. The *p*-chlorophenylaminosulphonates, when heated at 230—250°, are converted into *p*-chloroaniline-*o*-sulphonates by a transference of the SO_3H group from the nitrogen atom of the aniline to a carbon atom of the benzene ring in the ortho-position relatively to the amino-group.

p-Chloroaniline aminosulphonate, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH}_2 \cdot \text{NH}_2 \cdot \text{SO}_3\text{H}$, prepared by adding finely powdered aminosulphonic acid to an alcoholic solution of *p* chloroaniline, crystallises from absolute alcohol in large, lustrous leaflets melting at 160°. Ammonium *p*-chlorophenylaminosulphonate, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{SO}_3\text{NH}_4$, prepared by heating aminosulphonic acid with excess of *p*-chloroaniline, crystallises from alcohol in colourless, lustrous plates melting and decomposing at about 205°; the *p*-chloroaniline salt, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{SO}_3\text{H} \cdot \text{C}_6\text{H}_4\text{Cl} \cdot \text{NH}_2$, prepared by heating *p*-chloroaniline aminosulphonate at 160°, crystallises from alcohol in star-shaped aggregates of white needles decomposing at 190°; the barium salt, prepared by treating *p*-chloroaniline *p*-chlorophenylaminosulphonate with excess of concentrated aqueous barium hydroxide, crystallises in white needles and decomposes quantitatively into *p*-chloroaniline, sulphuric acid, and barium sulphate when boiled with hydrochloric acid; the silver salt is only obtainable from the free acid and silver carbonate and crystallises in white needles. *p*-Chlorophenylaminosulphonic acid, prepared from the barium salt, crystallises in concentric groups of white needles, which decompose at about 200°; on treatment with nitrous acid, it is converted into *p*-dichlorodiazaminobenzene.

4-Chloroaniline-2-sulphonic acid is formed on heating *p*-chloroaniline aminosulphonate at 250°, but is best prepared by heating aminosulphonic acid at 230° with excess of *p*-chloroaniline. It crystallises in anhydrous needles or colourless plates, and decomposes at 280° (compare Claus and Mann, *Abstr.*, 1891, 1488). The barium salt crystallises in prisms, and the silver salt in small needles.

The diazo-compound, $\text{C}_6\text{H}_3\text{Cl} \begin{array}{c} \text{N}_2 \\ | \\ \text{SO}_2 \end{array} > \text{O}$, crystallises in pale yellow needles and is extremely stable; only by heating with alcohol under pressure at 110° is it converted into *m*-chlorobenzenesulphonic acid. The barium salt of this acid is found to crystallise with $1\frac{1}{2}\text{H}_2\text{O}$ (compare Kieselinsky, *this Journ.*, 1876, i, 930).

Only once was a small quantity of 4-chloroaniline-3-sulphonic acid formed together with its isomeride on heating *p*-chloroaniline with

aminosulphonic acid. The barium salt of this acid was found to crystallise with $5\text{H}_2\text{O}$ (compare Claus and Mann, *loc. cit.*); the silver salt forms short needles; the *diazo*-compound crystallises in white needles and is very stable. K. J. P. O.

Thiosulphonic Acids of Aromatic Amines and *m*-Diamines. CLAYTON ANILINE CO. (D.R.-P. 120504).—Aniline *o*-disulphide, $(\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$, the main product of the action of sulphur on aniline, when suspended in water and treated with excess of sulphur dioxide, yields aniline-*o*-thiosulphonic acid, a substance crystallising from water in colourless needles. This product, when boiled in acid or alkaline solutions, loses the elements of sulphur dioxide and regenerates the disulphide.

Aniline *p*-disulphide (Hofmann, Abstr., 1895, i, 87) yields aniline-*p*-thiosulphonic acid. Dimethylaniline disulphide also gives rise to the thiosulphonic acid on treatment with sulphur dioxide; this acid yields a nitroso-derivative and is readily decomposed by acids or alkalis, regenerating the disulphide.

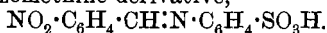
m-Phenylenediamine and 2:4-tolylenediamine, when heated with sulphur at 60 – 120° , yield mixtures containing basic and non-basic constituents. The former, when treated with sulphur dioxide, give soluble derivatives, which are probably monothiosulphonic acids, whilst the latter yield dithiosulphonic acids. The *m*-phenylenediamine derivatives separate in colourless crystals, the corresponding tolylenediaminedithiosulphonic acid has not been obtained in a crystalline state. G. T. M.

Condensation Products of Aromatic Aldehydes with Primary Aromatic Amines and their Sulphonic Acids. JOHANN WALTER (D.R.-P. 118567).—Compounds of the benzylidene-aniline type (azomethine derivatives $\text{R}\cdot\text{CH}\cdot\text{NR}'$) are obtained by oxidising a mixture of a tertiary base or a phenol and formaldehyde in the presence of an aromatic primary base or its sulphonic acid.

An aqueous solution of phenol, formaldehyde, and sodium *p*-toluidine-sulphonate, when oxidised with cupric chloride, yields a precipitate consisting of sodium *p*-hydroxybenzylidene-*p*-toluidinesulphonate, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_3\text{Na}$, and its *o*-isomeride. These azomethine derivatives are hydrolysed by acids, yielding the corresponding aldehydes. The compound $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}\cdot\text{N}\cdot\text{C}_7\text{H}_7$ results from the interaction of β -naphthol, formaldehyde, *p*-toluidine hydrochloride, and sodium chromate; it crystallises in pale yellow leaflets and when hydrolysed by mineral acids yields *p*-toluidine and β -hydroxynaphthaldehyde, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHO}$.

A mixture of dimethylaniline, formaldehyde, sodium *p*-toluidine-sulphonate, and potassium dichromate gives rise to the compound $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_7\text{H}_6\cdot\text{SO}_3\text{H}$, this substance on hydrolysis with acids yielding *p*-dimethylaminobenzaldehyde.

p-Nitrobenzyl alcohol, when oxidised in the presence of sulphanilic acid, furnishes the azomethine derivative,



Similar condensation products of benzidine are obtained by treating this base either with homosalignin, or with ethylaniline and form-

aldehyde in presence of an oxidising agent. When these products are hydrolysed, homosalicylaldehyde and *p*-ethylaminobenzaldehyde are respectively set free.
G. T. M.

New Class of Organic Compounds. *iso*Nitriles and *cyclo*-Nitriles. By ALEXANDER P. SABANÉEFF and M. PROSIN (*Bull. Soc. Chim.*, 1901, [iii], 25, 823—828).—When a mixture of aniline with acetylene dibromide, acetylene tetrabromide, or bromoacetylene dibromide is treated with alcoholic potash, acetylenetriphenyltri-amine, $C_2H_2(NHPh)_3 \cdot NPh$, and *phenyldicarbylamine*, $\begin{smallmatrix} C \\ || \\ C \end{smallmatrix} > NPh$, are produced.

The latter substance was obtained as an oily liquid which readily oxidised on exposure to air with the formation of a crystalline compound, $\begin{smallmatrix} CO \\ | \\ CO \end{smallmatrix} > NPh$, convertible into oxanilic acid on treatment with water. On heating with sulphur, phenyldicarbylamine is converted into dithio-oxanilide and *dithio-oxanil*, $\begin{smallmatrix} CS \\ | \\ CS \end{smallmatrix} > NPh$, which, however, could not be obtained in the pure state. When heated with copper powder at 200—205°, dithio-oxanil yields a substance which is probably the nitrile, $\begin{smallmatrix} N \\ | \\ C \end{smallmatrix} > CPh$, isomeric with phenyldicarbylamine.
N. L.

Preparation of 4-Nitro- α -Naphthylamine and its Alkyl Derivatives from 1-Chloro-4-nitronaphthalene. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P., 117006. Compare Eng. Pat. 7692 of 1900).—1-Chloro-4-nitronaphthalene, when heated at 180—200° with an alcoholic solution of ammonia, ethylamine, or benzylamine, yields either 4-nitro- α -naphthylamine or the corresponding *ethyl* or *benzyl* derivative. The former of these secondary amines crystallises in dark red needles melting at 176—177° and having a blue fluorescence, whilst the latter melts at 156°. This reaction does not occur when the chlorine atom is situated in positions 5 or 8 with respect to the nitro-group.
G. T. M.

Transformation of Hydroxynaphthalene Derivatives into the Corresponding Amines. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 117471).—The formation of amines from phenols is greatly facilitated when the ammonia reacts in the presence of ammonium sulphite; a mixed sulphite, $OR \cdot SO_2 \cdot NH_4$, is formed as an intermediate product, and this is subsequently converted by the excess of ammonia into the required amino-derivative, $R \cdot NH_2$. In the case of β -naphthol, the reaction takes place at 100—150°.

2:3-Dihydroxynaphthalene, when heated at 80° with ammonium sulphite solution and saturated with ammonia gives rise to a mixture of 2:3-aminohydroxynaphthalene and the corresponding diamine. 1:5-Dihydroxynaphthalene, when heated with these reagents at 125°, yields 1:5-diaminonaphthalene; this base is also obtained from 5-amino- α -naphthol.

Sodium α -naphthol-4-sulphonate at 100—150° yields α -naphthyl-

amine-4 sulphonic acid. The sulphite of α -naphthol-7-sulphonic acid readily yields α -naphthylamine-7-sulphonic acid when heated at 100—110° with excess of ammonia (compare Eng. Pat. 1387 of 1900). 1:5-Dihydroxynaphthalene-7-sulphonic acid, when subjected to this process, furnishes the corresponding aminonaphtholsulphonic acid.

Resorcinol behaves like the dihydroxynaphthalenes and gives either *m*-aminophenol or *m*-phenylenediamine, according to the quantities of ammonia and sulphite employed.

G. T. M.

8:8'-Dihydroxy-2:2'-dinaphthylamine-6:6'-disulphonic Acid. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 121094. Compare D.R.-P. 114974).—8:8'-*Dihydroxy-2:2'-dinaphthylamine-6:6'-disulphonic acid*, $\text{NH}[\text{C}_{10}\text{H}_6(\text{OH})\cdot\text{SO}_3\text{H}]_2$, prepared by heating sodium 8-hydroxy- β -naphthylamine-6-sulphonate with water at 200°, is a white, crystalline substance readily dissolving in water and forming soluble alkali salts which are precipitated by sodium chloride. The aqueous solution of the sodium salt exhibits a faint violet fluorescence.

G. T. M.

Phenanthrylamines. By ALFRED WERNER and J. KUNZ (*Ber.*, 1901, **34**, 2524—2528).—When 3-hydroxyphenanthrene (3-phenanthrol) (Pschorr and Sumuleanu, *Abstr.*, 1900, i, 488) is heated with sodium acetate, ammonium chloride, and glacial acetic acid for 9 hours at 280—300°, 3-acetylaminophenanthrene (*acetyl-3-phenanthrylamine*) is obtained in yield equal to 75 per cent. of the theoretical. It melts at 200—201°, and when hydrolysed yields 3-aminophenanthrene (3-*phenanthrylamine*), β , which melts at 87.5°. An isomeric 3-aminophenanthrene, α , melting at 143°, is obtained in 15 per cent. yield when the hydroxyphenanthrene is heated with aqueous ammonia and ammonium chloride at 200—220°. Each isomeride forms a hydrochloride and is regenerated unchanged from this; when treated with acetic anhydride, however, both yield the same acetyl derivative, described above.

When phenanthrene is sulphonated according to Graebe's directions, an insoluble barium sulphonate is formed amongst other products. From this, 2-hydroxyphenanthrene (2-phenanthrol) melting at 169° can be prepared. When the last substance is heated with sodium acetate, ammonium chloride, and acetic acid at 290°, 2-acetylaminophenanthrene (*acetyl-2-phenanthrylamine*) is obtained in 50 per cent. yield. It melts at 225—226° and is hydrolysed by hydrochloric acid in strong acetic acid solution at 100° to 2-aminophenanthrene (2-*phenanthrylamine*), which melts at 85°.

It was not found possible to diazotise either of the aminophenanthrenes.

C. F. B.

Phenyl Carbonates. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 117346. Compare *Farbenfabriken vorm. F. Bayer & Co.*, this vol., i, 662).—The additive compounds of the pyridine bases with carbonyl chloride react with the phenols, yielding the corresponding phenyl carbonates. The pyridine carbonyl chloride compound, when treated in benzene or xylene solution with phenol or *o*-cresol, gives rise to phenyl carbonate or *o*-tolyl carbonate respectively; guaiacol carbonate may be similarly

prepared. The analogous derivatives of 2-lutidine and 2-picoline behave in a similar manner. G. T. M.

Chlorocarbonates of Alcohols, Phenols, and their Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 118536. Compare this vol., i, 662, and D.R.-P. 114025).—The chlorocarbonates, $\text{RO}\cdot\text{COCl}$, may be prepared by the action of carbonyl chloride on the corresponding hydroxy-compound, $\text{R}\cdot\text{OH}$, in the presence of antipyrine or one of its analogues dissolved in benzene. Ethyl, benzyl, and phenyl chlorocarbonates are readily obtained in this manner. G. T. M.

Chlorocarbonates of Alcohols and Phenols and their Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 118537. Compare preceding abstract, and D.R.-P. 109933 and 114025).—*Salol chlorocarbonate*, $\text{CO}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{COCl}$, prepared by the interaction of salol and hexachlorodimethyl carbonate in a xylene solution of quinoline, separates from light petroleum in white crystals and melts at $90-91^\circ$. The hexachlorodimethyl carbonate may be replaced by carbonyl chloride or perchloromethyl formate, and other tertiary bases, such as antipyrine or dimethylaniline, may be substituted for quinoline; the bases of the pyridine series, however, are not suitable for this reaction. G. T. M.

Physical Isomerism of Thallium Picrate. By W. O. RABE (*Zeit. physikal. Chem.*, 1901, 38, 175—184).—When thallium picrate is crystallised from 96 per cent. alcohol, a mass of slender yellow needles is first thrown down. If these are left a few days in contact with the solution, small, red, shining crystals are formed between the yellow ones. Analysis and examination of their properties show that both the yellow and the red crystals are thallium picrate. The two modifications differ, not only in colour, but in specific gravity, in crystalline form, and in solubility. The sp. gr. of the yellow crystals (as determined by the suspension method) is 2.993 at 17° , that of the red crystals is 3.164 at 17° . The yellow crystals are thin, long needles, whilst the red crystals are either long prisms or plates; the crystallographic measurements are recorded in the paper. The difference of solubility (whether in water or methyl alcohol) is not large, but the solubility curves for both solvents cut each other at 46° , which is therefore the temperature of transition of the red into the yellow modification. When heated at 130° , the red crystals are transformed into the yellow crystals in a few seconds; the reverse change takes place very slowly below 40° , but is accelerated by light or the presence of a little solvent. J. C. P.

Action of Bromine on Carvacrol in the Presence of Aluminium Bromide. By F. BODROUX (*Bull. Soc. Chim.*, 1901, [iii], 25, 818).—The action of bromine on carvacrol in the presence of aluminium bromide leads to the formation of nearly the theoretical quantity of *tetrabromo-o-cresol*, which crystallises in long, white, silky needles melting at 208° . N. L.

Primary Aminobenzohydrols. KALLE & Co. (D.R.-P. 119461).—Aminobenzohydrols are produced by heating either a mixture of an

aromatic aldehyde and a primary base or the corresponding azomethine derivative in an alcoholic solution of a mineral acid. 4-Nitro-4'-amino-benzohydrol, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, produced in this way either from *p* nitrobenzylideneaniline or a mixture of its generators, forms a yellow, crystalline powder, melts at 240° , and is insoluble in the ordinary solvents, but dissolves readily in a mixture of glacial acetic and hydrochloric acids.

G. T. M.

Preparation of 4-Nitro- α -naphthol and its Ethers from 1-Chloro-4-nitronaphthalene. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 117731).—1-Chloro-4-nitronaphthalene, when heated at 150 — 155° with sodium hydroxide dissolved in dilute alcohol, yields 4-nitro- α -naphthol; the methyl and ethyl ethers of this naphthol are obtained when the reaction is performed in methyl and ethyl alcohols respectively.

G. T. M.

α -Naphthol Ethyl Ether and its Derivatives. By OTTO N. WITT and FRANZ SCHNEIDER (*Ber.*, 1901, 34, 3171—3191).—Details are given for preparing 1-ethoxynaphthalene from α -naphthol and potassium ethyl sulphate, this method being more advantageous than direct ethylation by means of alcohol and sulphuric acid (Gattermann, *Annalen*, 1888, 244, 72); the ether, as obtained hitherto, has always been contaminated with α -naphthol, and the last traces of the latter are only removed by distilling in a vacuum and adding sufficient diazobenzenesulphonic acid and dilute alkali to form the tetrazo-dye derived from the naphthol. Thus purified, 1-ethoxynaphthalene melts at 5.5° , and boils at 276.4° (corr.) under 760 mm., at 276.6° (corr.) under 766 mm., at 185° (corr.) under 19 mm., and at 106 — 106.5° under 2 mm. pressure. The refractive indices for the principal lines of the spectrum are given; n_D is 1.59916, and the dispersion quotient is 21.0; the sp. gr. at 19° is 1.061.

Heermann's method of preparing 1-ethoxynaphthalene-4-sulphonic acid (*Abstr.*, 1894, i, 251) is modified on account of the need of removing unchanged naphthol ether from the product; the sulphonic acid and its salts dissolve this in considerable quantity, and it is best removed by extracting the acid thoroughly with chloroform. The pure acid is crystallised from water at 50° , and forms large, four-sided plates with $2\text{H}_2\text{O}$, which become anhydrous in a desiccator; the ammonium salt is anhydrous, the potassium crystallises with $1\text{H}_2\text{O}$, the sodium salt with $5\text{H}_2\text{O}$ or anhydrous, the barium salt with $1\text{H}_2\text{O}$, and the strontium salt with $2\text{H}_2\text{O}$. 1-Ethoxynaphthalene-4-sulphonic chloride crystallises from ether or light petroleum in six-sided, yellowish plates, and melts at 101° ; the sulphonamide crystallises from alcohol in stout, white needles, and melts at 167° ; the sulphanilide, from the same solvent, forms flat needles and melts at 178° . The ethyl ester forms long prisms melting at 102 — 103° , and the methyl ester colourless leaflets melting at 105 — 106° .

By cold acetic anhydride, the sulphonic acid is converted into the mixed anhydride, $\text{OEt} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_2 \cdot \text{OAc}$, which forms thick, transparent crystals, is decomposed by water and alcohol, and in the air is transformed, initially, apparently into the anhydride, $\text{O}_2(\text{SO}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OEt})_2$, with loss

of acetic anhydride, and ultimately into 1-ethoxynaphthalene-4-sulphonic acid.

Phenylnaphthionic acid, $\text{NHPh} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{H}$, is better obtained by first gently warming and then boiling a solution of 1-ethoxy-4-naphthalenesulphonic acid in an excess of aniline for a quarter of an hour, than by the German Patent 70349; if, however, the solution is boiled too long, sulphanilic acid and α -naphthylphenylamine are formed, whilst if the solution of the acid in aniline is boiled at once after being made, sulphanilic acid and α -naphthol ethyl ether are formed without any phenylnaphthionic acid. Similar results were obtained with *p*-toluidine; *p*-tolyl-naphthionic acid crystallises from water in long, rectangular, anhydrous plates and melts at 194° .

Instead of yielding 4-nitro-1-ethoxynaphthalene alone, the action of nitric acid (1 mol.) on 1-ethoxynaphthalene-4-sulphonic acid (compare Heermann, *loc. cit.*) gives a molecular compound of it with dinitro- α -naphthol; by adding carbamide, however, to the nitric acid, even if the latter be in excess, the formation of dinitro- α -naphthol is prevented, and 4-nitro-1-ethoxynaphthalene is obtained along with 2-nitro-1-ethoxynaphthalene-4-sulphonic acid. The potassium salt of the latter crystallises in large, thick plates and prisms, and when heated with concentrated hydrochloric acid at 150 – 160° for 2 hours, yields 2-nitro- α -naphthol, thus proving the constitution of the acid. Using boiling concentrated aqueous potassium hydroxide for the hydrolysis, dipotassium 2-nitro- α -naphthol-4-sulphonate is obtained in orange-yellow, silky needles or thick prisms; the monopotassium salt forms long, lemon-yellow needles. The barium salt, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_5 \cdot \text{SO}_3 \cdot \text{Ba} \cdot 2\text{H}_2\text{O}$, is very sparingly soluble in water, and the scarlet lead salt is similar. W. A. D.

8-Hydroxy- α -naphthylamine-4-sulphonic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 120016).—The sulphurous ester, $\text{SO}_3\text{H} \cdot \text{C}_{10}\text{H}_5(\text{NH}_2) \cdot \text{O} \cdot \text{SO}_2\text{H}$, is produced on heating 1:8-diaminonaphthalene-4-sulphonic acid with either the bisulphite compound of acetone or a mixture of sodium, hydrogen sulphite, acetone, and sodium hydroxide, the reaction being carried out in concentrated aqueous solutions; the ester is very soluble in water, and, unlike the hydroxynaphthylaminesulphonic acid, yields a normal diazonium derivative which combines with phenols forming azo-colouring matters.

8-Hydroxy- α -naphthylamine-4-sulphonic acid is obtained on hydrolysing the preceding compound with alkali hydroxides. G. T. M.

2:3-Dicyanoquinol. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P. 117005).—2:3-Dicyanoquinol, prepared by adding a concentrated potassium cyanide solution to a solution of quinone in alcoholic sulphuric acid and precipitating with excess of acid, crystallises from water in yellow needles. Two mols. of the quinone take part in the reaction, the second being reduced to quinol. When warmed with concentrated sulphuric acid, the dicyanoquinol yields *p*-dihydroxyphthalimide. G. T. M.

IsoChavibetol. CÆSAR POMERANZ (D.R.-P. 119253).—Propenylcatechol ethoxymethyl ether, $\text{CHMe} \cdot \text{CH} \cdot \text{C}_6\text{H}_4(\text{OMe}) \cdot \text{O} \cdot \text{CH}_2 \cdot \text{OEt}$, the

methyl ether of ethoxyisoeugenol, results from the methylation of the latter phenol by the action of methyl iodide and aqueous sodium hydroxide solution; it is a colourless, refractive liquid boiling at 160—162° under 14 mm. pressure.

iso*Charibetol*, $\text{CHMe}:\text{CH}\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{C}(\text{OH}) \\ \text{CH}-\text{CH} \end{smallmatrix}\text{C}\cdot\text{OMe}$, produced by heating the preceding compound with a dilute solution of hydrochloric acid in alcohol and water, melts at 92° and boils at 147° under 14 mm. pressure; it has a pleasant odour resembling that of vanilla and clove.

G. T. M.

Tetrahydrodiphenylene Oxide. By OTTO HÖNIGSCHMID (*Monatsh.*, 1901, 22, 561—576).—*Tetrahydrodiphenylene oxide*, $\text{C}_{12}\text{H}_{12}\text{O}$, is prepared by reducing diphenylene oxide by excess of sodium and absolute alcohol, and is a heavy, colourless oil, boiling at 268—269°, which dissolves in sulphuric acid with a red colour; from this solution, water throws down a bluish-violet oil. The *picrate*, $\text{C}_{18}\text{H}_{15}\text{O}_8\text{N}_3$, crystallises in orange-yellow needles melting at 91°. When a smaller quantity of sodium is used in the reduction, a mixture of crystals melting at 43° and oil is obtained; in this mixture probably unchanged diphenylene oxide and dihydrodiphenylene oxide are present, together with the tetrahydro-derivative.

Tetrahydrodiphenylene oxide is oxidised by potassium permanganate to diphenylene oxide; by fused potassium hydroxide, it is converted into 1-hydroxydiphenyl (m. p. 56°; compare Graebe, *Abstr.*, 1895, i, 372).

1-*Hydroxydiphenyl acetate*, $\text{C}_{12}\text{H}_9\cdot\text{OAc}$, crystallises in colourless needles. 1-*Ethoxydiphenyl*, $\text{C}_{12}\text{H}_9\cdot\text{OEt}$, crystallises in lustrous prisms melting at 34° and boiling at 276°; the *methoxy*-derivative forms lustrous prisms melting at 29° and boiling at 274°.

By treating an additive product of tetrahydrodiphenylene oxide and bromine with alcoholic potash, hydrogen bromide is eliminated, and a small quantity of an oil is obtained which boils at 278° and is probably dihydrodiphenylene oxide.

In attempting to prepare phenylene- α -naphthylene oxide by Arx's method (*Abstr.*, 1881, 282), the author obtained only a dinaphthylene oxide (m. p. 178—179°) which has properties identical with those hitherto ascribed to phenylene- α -naphthylene oxide. On reduction with sodium and amyl alcohol, *octahydrodinaphthylene oxide*, $\text{C}_{20}\text{H}_{20}\text{O}$, is formed, crystallising in colourless needles which melt at 128° and exhibit a feeble blue fluorescence.

K. J. P. O.

Alkylation of Hydroxyquinol [1:2:4-Hydroxybenzene]. By E. BREZINA (*Monatsh.*, 1901, 22, 590—600. Compare this vol., i, 534).—The action of ethyl bromide or iodide and potassium hydroxide on 1:2:4-triacetoxybenzene yields a yellow oil insoluble in potassium hydroxide. When this oil was distilled under a pressure of 20 mm., distillation began at 150° and was stopped at 200°, on the appearance of signs of decomposition.

From the residue there separated crystals of *hexaethoxydiphenyl*, $\text{C}_{12}\text{H}_4(\text{OEt})_6$, representing 2.5 to 2.7 per cent. of the triacetoxybenzene used. This compound crystallises in triclinic plates or white needles

melting at 100—102°, and dissolving in sulphuric acid with a red colour which becomes green on heating. On treatment with hydriodic acid, a *hexahydroxydiphenyl* is obtained which decomposes at about 200°, and does not appear to be identical with δ -hexahydroxydiphenyl (Barth and Schreder, Abstr., 1885, 520). On acetylation, two substances are formed, a hexa-acetoxydiphenyl (m. p. 169—172°), probably identical with the acetyl derivative of δ -hexahydroxydiphenyl, and *tetra-acetoxydiphenylene oxide*, $C_{12}H_4O(OAc)_4$, which melts at 240—245°.

From the distillate, triethoxybenzene separated on cooling; the remaining oil was fractionated under 15 mm. pressure. The first fraction boiling at 130—135°, was mainly 1 : 4-diethoxybenzene (m. p. 68—70°). From the fraction boiling at 155—165° was isolated *triethoxyethylbenzene*, $C_6H_2Et(OEt)_3$, which forms crystals melting at 31—32° and boils at 157—160° under 18 mm. pressure. *Dibromotriethoxyethylbenzene*, $C_6Br_2Et(OEt)_2$, prepared from the last-mentioned compound, forms crystals melting at 65—67°.

K. J. P. O.

Derivatives of Hydroxyquinol. By JOHANNES THIELE and KARL JAEGER (*Ber.*, 1901, **34**, 2837—2842).—The *tribenzoyl* derivative of hydroxyquinol crystallises in lustrous leaflets, melts at 120°, and is hydrolysed much less readily than the triacetyl derivative. Hydroxyquinol, when treated with nitric acid, yields oxalic acid, but the triacetyl derivative gives nitranilic acid. When the triacetyl derivative is nitrated in the presence of acetic anhydride, a *nitro*-derivative, $C_{12}H_{11}O_8N$, is obtained, which crystallises from dilute alcohol in long, white needles and melts at 107—108°; when hydrolysed, it yields *nitrohydroxyquinol*, $C_6H_5O_5N$, which forms yellowish-red crystals decomposing between 200° and 220°, and when treated with bromine is converted into tribromohydroxyquinone.

Dibromonitrohydroxyquinol, $C_6H_3O_5NBr_2$, obtained by treating nitrohydroxyquinol dissolved in carbon disulphide with bromine, crystallises from benzene in microscopic needles and melts and decomposes at 164°. *Tribromohydroxyquinol*, $C_6H_3O_5Br_3$, obtained by reduction of tribromohydroxyquinone, crystallises from benzene in small, reddish needles which turn brown at 110° and decompose at 120°, and forms a *triacetyl* derivative which crystallises in white needles and melts at 189°.

Hydroxyquinolcarboxylic acid, $C_7H_6O_6$, obtained by the action of sodium hydrogen carbonate and carbon dioxide on the hydroxyquinol, crystallises from water in needles with $\frac{1}{2}H_2O$, melts and decomposes at 217—218°, gives a greenish coloration with concentrated sulphuric acid, and forms a *triacetyl* derivative which crystallises in plates or needles and melts at 162—163°. When reduced with sodium amalgam, both hydroxyquinol and hydroxyquinolcarboxylic acid yield the dihydroresorcinol described by Merling (Abstr., 1894, i, 177).

R. H. P.

p-Hydroxytriphenylcarbinol. By AUGUSTIN BISTRZYCKI and CARL HERBST (*Ber.*, 1901, **34**, 3073—3079. Compare this vol., i, 716).—*p*-Hydroxytriphenylcarbinol, $OH \cdot C_6H_4 \cdot CPh_2 \cdot OH$, is produced when *p*-hydroxytriphenylacetic acid is slowly added to cold concentrated

sulphuric acid, the action being accompanied by an evolution of carbon monoxide; it crystallises from dilute acetic acid, or from benzene and petroleum, in pale yellow or colourless plates, and decomposes at 70° . At this temperature, 2 mols. of the substance lose the elements of water, and yield *p*-hydroxytriphenylmethyl ether, $O(CPh_2 \cdot C_6H_4 \cdot OH)_3$, a substance crystallising from ether in needles and melting at 70° . The ether closely resembles the carbinol in physical properties, and is readily transformed into the latter compound on treatment with dilute acetic acid; both substances are soluble in warm potassium hydroxide solutions. *p*-Acetoxytriphenylcarbinol, $OAc \cdot C_6H_4 \cdot CPh_2 \cdot OH$, obtained by warming the carbinol with acetic anhydride and dry sodium acetate, crystallises in small plates and melts at 136° ; it is insoluble in cold dilute potassium hydroxide solution.

p-Acetoxytriphenylmethyl ether, $O(CPh_2 \cdot C_6H_4 \cdot OAc)_2$, produced either by acetylating *p*-hydroxytriphenylmethyl ether or by treating the corresponding carbinol with acetic anhydride containing a trace of sulphuric acid, crystallises in hexagonal plates and melts at $136-137^{\circ}$. It closely resembles the preceding compound.

p-Benzoyloxytriphenylcarbinol, $OBz \cdot C_6H_4 \cdot CPh_2 \cdot OH$, prepared by the Schotten-Baumann reaction, forms prisms melting at 132° ; like the corresponding acetoxy-compound, it is insoluble in solutions of the alkali hydroxides. The *m*-nitro-derivative crystallises in aggregates of needles and melts at 150° .

Dibromo-p-hydroxytriphenylcarbinol, $OH \cdot C_6H_2Br_2 \cdot CPh_2 \cdot OH$ and carbon monoxide are the products of the action of concentrated sulphuric acid on dibromo-*p*-hydroxytriphenylacetic acid at 50° . The carbinol crystallises from glacial acetic acid in four-sided plates and melts at 225° ; it is very sparingly soluble in dilute potassium hydroxide solution.

Dibromo-p-acetoxytriphenylmethyl ether, $O(CPh_2 \cdot C_6H_2Br_2 \cdot OAc)_2$, prepared by warming the preceding compound with acetic anhydride and sodium acetate, crystallises in plates and melts at 171° . G. T. M.

Carbinol Compounds of Triphenylmethane and its Derivatives. By JOSEF HERZIG and P. WENGRAF (*Monatsh.*, 1901, **22**, 601-614. Compare Abstr., 1894, i, 336; 1896, i, 486).—It has been shown that in the two triacetylaurins the presence of a hydroxyl group cannot be demonstrated, and it has been suggested that one of the benzene nuclei is in the quinone form and that, consequently, no hydroxyl group is present (*loc. cit.*). Similar observations have been made by Döbner in the case of benzaurin (Abstr., 1883, 861). The ethyl derivatives of tetramethyldiaminotriphenylcarbinol and of hexamethyltriaminotriphenylcarbinol are, however, true ethoxy-compounds.

Although with alcohol and dilute acids (best a 3 per cent. alcoholic solution of hydrogen chloride) triphenylcarbinol yields an ethoxy-derivative with great ease, with alkalis and alkyl iodide, no alkyl derivative can be prepared. The alkyl ethers are readily hydrolysed by acids, but not by alkalis. The acetyl derivative (Allen and Kölliker, Abstr., 1885, 655), by mere recrystallisation from alcohol, is quantitatively transformed into the ethyl ether,

whilst the latter, by the action of acetic anhydride or acetyl chloride, can be converted into the acetyl derivative. The carbinol itself can only be acetylated by means of acetyl chloride. In these properties, triphenylcarbinol does not resemble any known hydroxyl compounds.

In the acetylation of rosolic acid by sodium acetate and acetic anhydride, besides the *triacetate*, $C_{20}H_{15}O_5Ac_3$ (crystals melting at $167-168^\circ$), there was obtained a very small quantity of a substance melting at $144-146^\circ$. From benzaurin, on acetylation, a *diacetate*, $C_{19}H_{14}O_3Ac_2$, is readily obtained, which melts at $144-146^\circ$, and on reduction with zinc and acetic acid yields diacetoxytriphenylmethane (m. p. $108-110^\circ$). Döbner (*loc. cit.*) describes a diacetate of benzaurin which melts at $116-119^\circ$; the authors were only able to obtain this compound once in ten attempts.

K. J. P. O.

Mixed Acid Anhydrides. KNOLL & Co. (D.R.-P. 117267).—The mixed anhydrides of the organic acids are readily prepared by mixing an acid or its salt with an acid chloride dissolved in an indifferent solvent containing a tertiary base. Benzoyl acetate is obtained from acetyl chloride and benzoic acid or benzoyl chloride and acetic acid in the presence of pyridine, and boils at $125-140^\circ$ under 17 mm. pressure. Under similar conditions, *ethyl benzoyl carbonate*, $Bz \cdot CO_2Et$, and *dibenzoyl carbonate*, $COBz_2$, are produced by the interaction of benzoic acid with ethyl chlorocarbonate and carbonyl chloride respectively; these compounds are oils, the latter readily decomposing into carbon dioxide and benzoic anhydride.

The action of ethyl chlorocarbonate on salicylic acid gives rise to two compounds, *ethyl salicyl monocarbonate*, $CO_2H \cdot C_6H_4O \cdot CO_2Et$, and *diethyl salicyl dicarbonate*, $CO_2Et \cdot O \cdot C_6H_4 \cdot CO_2 \cdot CO_2Et$; the latter is a neutral oil. *Ethyl cinnamyl carbonate*, $CHPh \cdot CH \cdot CO_2 \cdot CO_2Et$, and *ethyl valeryl carbonate* and valeryl acetate are produced in a similar manner. Quinoline or dimethylaniline may be employed instead of pyridine.

G. T. M.

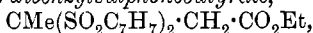
Disulphones. VII. Mercaptoles and Disulphones of the Ketonic Acids and the Sulphur Acids obtained from them. By THEODOR POSNER (*Ber.*, 1901, 34, 2643—2673. Compare *Abstr.*, 1900, i, 5).—The nature and stability of the mercaptoles and disulphones formed from the ketonic esters and the mercaptans are influenced both by the nature of the mercaptan and by that of the ketonic ester. Derivatives of the substituted esters are both less easily produced and less stable. Characteristic differences also show themselves in the behaviour on hydrolysis.

[With ALEX. DEINHARDT.]—Lævulic acid readily undergoes condensation with benzyl mercaptan in acetic acid solution in presence of hydrogen chloride, with formation of γ -*dithiobenzylvaleric acid* (lævulic benzylmercaptole), $CMe(SC_7H_7)_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, melting at 70° . Oxidation converts it into γ -*dibenzylsulphonevaleric acid* (lævulic benzylidisulphone), $CMe(SO_2 \cdot C_7H_7)_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, which crystallises in silky needles and plates and melts and decomposes at $143-145^\circ$. With amyl mercaptan, lævulic acid yields γ -*dithioamylvaleric acid*, $CMe(SC_5H_{11})_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, which can only be

obtained as an oil. The corresponding γ -diamylsulphonevaleric acid, $\text{CMe}(\text{SO}_2\cdot\text{C}_5\text{H}_{11})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, crystallises in slender needles melting at $98-100^\circ$; the barium salt is sparingly soluble. γ -Dithiophenylvaleric acid, $\text{CMe}(\text{SPh})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, crystallises in rectangular tablets, probably belonging to the monoclinic system, which melt at 67° . On oxidation with permanganate in acetic acid solution, it yields γ -diphenylsulphonevaleric acid, $\text{CMe}(\text{SO}_2\text{Ph})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, as a crystalline powder melting at 140° .

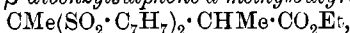
Ethyl lævulate also reacts with the mercaptans, yielding the ethyl esters of the acids just described, and these are converted by oxidation into the corresponding sulphones. All these esters are converted by hydrolysis into the corresponding acids. Ethyl γ -dithiobenzylvalerate, $\text{CMe}(\text{SC}_7\text{H}_7)_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is an oil, whilst ethyl γ -dibenzylsulphonevalerate forms slender crystals melting at $118-119^\circ$. Ethyl γ -dithioamylvalerate is a colourless oil, whilst ethyl γ -diamylsulphonevalerate crystallises in triclinic prisms melting at 46° . Ethyl γ -dithiophenylvalerate is also an oil, whilst ethyl γ -diphenylsulphonevalerate forms small crystals melting at $112-113^\circ$.

The derivatives of ethyl acetoacetate differ from those of ethyl lævulate in their behaviour on hydrolysis, unsaturated compounds being formed. Ethyl β -dithiobenzylbutyrate, $\text{CMe}(\text{SC}_7\text{H}_7)_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is an oil, and yields on hydrolysis β -thiobenzylisocrotonic acid, $\text{C}_7\text{H}_7\cdot\text{S}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, which melts at 125° and decomposes at $146-150^\circ$. Ethyl β -dibenzylsulphonebutyrate,



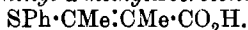
forms a loose, easily electrified powder, which sinters at $138-139^\circ$, and melts at $141-142^\circ$. On hydrolysis, it yields some benzyl mercaptan, together with an oily acid which slowly decomposes, yielding a neutral substance which melts at $104-105^\circ$. The nature of these products has not yet been ascertained. Ethyl β -dithioamylbutyrate is also an oil, and is converted by hydrolysis into thioamylisocrotonic acid, $\text{C}_5\text{H}_{11}\cdot\text{S}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, which crystallises in prisms melting at 96° . Ethyl β -diamylsulphonebutyrate is a colourless oil; the only product of hydrolysis which could be isolated was amylsulphinic acid. The derivatives of phenyl mercaptan have previously been described by Baumann and Escales (Abstr., 1886, 879) and Autenrieth (Abstr., 1891, 204).

[With O. CLAUDIUS.]—The mercaptoles derived from alkylacetoacetic esters are only oxidised to sulphones with great difficulty. Ethyl β -dithiobenzyl- α -methylbutyrate, $\text{CMe}(\text{S}\cdot\text{C}_7\text{H}_7)_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, melts at 78° . On hydrolysis, it yields the corresponding acid, which melts at $131-133^\circ$. Ethyl β -dibenzylsulphone- α -methylbutyrate,



melts at 130° ; the only product of hydrolysis which could be isolated was benzoic acid. Ethyl β -dithioamyl- α -methylbutyrate is an oil, and yields no well characterised products on hydrolysis. Ethyl β -diamylsulphone- α -methylbutyrate is also an oil, and on hydrolysis yields an acid of the molecular formula, $\text{C}_{10}\text{H}_{12}\text{O}_4$, probably having the constitution $\text{CO}_2\text{H}\cdot\text{C}\begin{smallmatrix} \text{CH}_2\cdot\text{CMe} \\ \text{CMe}\cdot\text{CH}_2 \end{smallmatrix}\text{C}\cdot\text{CO}_2\text{H}$, which melts at 234° . This acid is dibasic, contains two ethylene linkings, and yields a tetrabromide

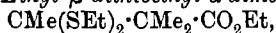
melting at 204° , whilst the *methyl ester* is crystalline and melts at 148° . *Ethyl β -dithiophenyl- α -methylbutyrate* melts at 49° and on hydrolysis yields *β -thiophenyl- α -methylisocrotonic acid*,



Ethyl β -diphenylsulphone- α -methylbutyrate melts at 130° and on hydrolysis yields an acid which could not be procured pure.

Ethyl β -dithiobenzyl- α -ethylbutyrate is an oil which on hydrolysis yields the saturated *β -dithiobenzyl- α -ethylbutyric acid* melting at $86-87^{\circ}$. The corresponding *sulphone*, $\text{CMe}(\text{SO}_2 \cdot \text{C}_6\text{H}_5)_2 \cdot \text{CHEt} \cdot \text{CO}_2\text{Et}$, melts at 97° , and yields benzoic acid on hydrolysis. *Ethyl β -dithioamyl- α -ethylbutyrate* is an oil and yields no definite compound on hydrolysis. The corresponding *sulphone* is also an oil, which is probably converted by hydrolysis into a mixture of amylsulphinic acid and *β -amylsulphone- α -ethylisocrotonic acid*. The mercaptole and disulphone of ethyl ethyl-acetoacetate and phenyl mercaptan have previously been described by Autenrieth. The mercaptole ester is converted by hydrolysis into *β -thiophenyl- α -ethylisocrotonic acid*, $\text{SPh} \cdot \text{CMe} : \text{CET} \cdot \text{CO}_2\text{H}$, which melts very indefinitely at $88-100^{\circ}$. The products of hydrolysis of the sulphone have not been isolated.

[With A. EBERS].—*Ethyl β -dithioethyl- α -dimethylbutyrate*,

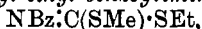


is a colourless oil; the corresponding *disulphone* crystallises in short, thick prisms melting at $131-133^{\circ}$, and is converted by hydrolysis into the free *acid*, which crystallises in microscopic needles and melts at $102-103^{\circ}$. *Ethyl β -dithiobenzyl- α -dimethylbutyrate* is a heavy oil, whilst the corresponding *disulphone* melts at $130-136^{\circ}$, and yields benzoic acid on hydrolysis. *Ethyl β -dithioamyl- α -dimethylbutyrate* and the corresponding *disulphone* are both oils. The condensation product of ethyl dimethylacetoacetate and phenyl mercaptan is converted by oxidation into phenyl disulphide, no disulphone being formed.

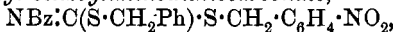
Ethyl β -dithioethyl- α -diethylbutyrate, $\text{CMe}(\text{SEt})_2 \cdot \text{CET}_2 \cdot \text{CO}_2\text{Et}$, is an unstable oil and is converted by oxidation into the *sulphone* which has not been obtained pure. The *benzylmercaptole* is also an oil, and is converted by oxidation into benzyl sulphone. The *amylmercaptole* is also an oil, and yields an oily *disulphone* which has not been obtained pure. The *phenylmercaptole* is an oil from which no disulphone could be obtained by oxidation, the only products isolated being phenyl disulphide and ethyl diethylacetoacetate. A. H.

Acetyl- and Benzoyl-iminodithiocarbonic Esters. By HENRY LORD WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1901, 26, 185—206).—*Methyl acetylaminodithiocarbonate*, $\text{NAc} : \text{C}(\text{SMe})_2$, prepared from sodium methyl acetylaminodithiocarbonate and methyl iodide in alcoholic solution, is an oil boiling at $142-144^{\circ}$ under 20 mm. pressure. *isoAmyl acetyldithiocarbamate*, $\text{NHAc} : \text{CS} \cdot \text{SC}_6\text{H}_{11}$, prepared from *isoamyl* thiocyanate and thioacetic acid, crystallises from alcohol in yellow plates and melts at 84° ; when dissolved in alcoholic sodium ethoxide and treated with *isoamyl* bromide, it gave *isoamyl acetyl-iminodithiocarbonate*, $\text{C}_{13}\text{H}_{25}\text{ONS}_2$, as an oil boiling at $198-200^{\circ}$ under 20 mm. pressure. Methyl benzoyliminodithiocarbonate, $\text{NBz} : \text{C}(\text{SMe})_2$, and the ethyl ester, are decomposed by hydrochloric acid to the mercap-

tan and methyl or ethyl benzoylthiolcarbamate, $\text{NHBz}\cdot\text{CO}\cdot\text{SMe}$, or $\text{NHBz}\cdot\text{CO}\cdot\text{SEt}$. *Methyl ethyl benzoyliminothiocarbonate*,

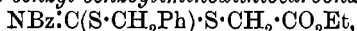


prepared from ethyl benzoyliminodithiocarbonate and methyl iodide or from the methyl ester and ethyl iodide, is an oil which boils at 224° under 20 mm. pressure and is apparently hydrolysed by hydrochloric acid to a mixture of methyl and ethyl benzoylthiolcarbamates; when warmed with aniline, it gave methyl and ethyl mercaptides, and a solid which crystallised from alcohol in flattened prisms, melted constantly at $79\text{--}80^\circ$, and appeared to be a mixture of the two compounds previously obtained in a similar manner from the dimethyl and diethyl compounds (Wheeler and Merriam, Abstr., 1901, i, 515). *Propyl benzoyliminothiocarbonate*, $\text{NBz}\cdot\text{C}(\text{SPr}^a)_2$, is a pale yellow oil which boils at $238\text{--}239^\circ$ under 20 mm. pressure. *isoAmyl benzoyldithiocarbamate*, $\text{NHBz}\cdot\text{CS}\cdot\text{SC}_5\text{H}_{11}$, crystallises from dilute alcohol in yellow prisms and melts at $48\text{--}49^\circ$. *Benzyl ethyl benzoyliminodithiocarbonate*, is an oil which does not crystallise and cannot be distilled without decomposition. The *dibenzyl* ester, $\text{NBz}\cdot\text{C}(\text{S}\cdot\text{CH}_2\text{Ph})_2$, crystallises from alcohol in long, silky needles, melts sharply at 97° , and has an odour suggestive of roses or carnations. *p-Nitrobenzyl benzoyliminodithiocarbamate*, $\text{NHBz}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, crystallises from alcohol in clusters of short, yellow needles, and melts at $155\text{--}156^\circ$. *p-Bromobenzyl benzoyldithiocarbamate*, $\text{NHBz}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Br}$, separates from alcohol as a yellow, crystalline powder and melts at 126° . *Benzyl-p-nitrobenzyl benzoyliminodithiocarbonate*,



crystallises from alcohol in short needles, and melts at $84\text{--}85^\circ$.

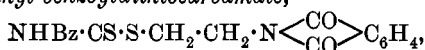
Carbethoxymethyl benzyl benzoyliminodithiocarbonate,



prepared from ethyl chloroacetate and benzyl benzoyldithiocarbamate, crystallises from alcohol in colourless, flattened prisms and melts at 79° . An isomeric compound, $\text{NHBz}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{Et}$, was, however, obtained on benzylating the carbethoxymethyl ester; this also melts at 79° , but a mixture of the isomerides melts at 63° ; it crystallises from alcohol in bunches of bright yellow prisms.

Phenyl thiocynoacetate, $\text{NCS}\cdot\text{CH}_2\cdot\text{CO}_2\text{Ph}$, prepared from phenyl chloroacetate and potassium thiocyanate, crystallises from dilute alcohol in colourless plates, sinters at 28° , and melts at $31\text{--}32^\circ$. *Carbophenoxyethyl benzoyldithiocarbamate*, $\text{NHBz}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Ph}$, crystallises from alcohol and melts at $127\text{--}129^\circ$. *α -Carbethoxyethyl benzyl benzoyliminodithiocarbonate*, $\text{NBz}\cdot\text{C}(\text{S}\cdot\text{CH}_2\text{Ph})\cdot\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, prepared from the monobenzyl ester and ethyl α -bromopropionate, forms colourless prisms and melts at $105\text{--}106^\circ$; the product from the interaction of benzyl chloride and the α derivative of ethyl propionate and benzoyldithiocarbamate melts at $105\text{--}106^\circ$, and appears to be isomeric with the preceding compound.

Phthaliminoethyl benzoyldithiocarbamate,



forms yellow needles and melts at $178\text{--}182^\circ$. By the action of benzyl chloride, it is converted into *phthaliminoethyl benzyl benzoyliminodithio-*

carbonate, $\text{NBz}\cdot\text{C}(\text{S}\cdot\text{CH}_2\text{Ph})\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}:(\text{CO})_2\cdot\text{C}_6\text{H}_4$, which crystallises from alcohol in colourless needles and melts at $119-120^\circ$; it could not be prepared from the benzyl compound and bromoethylphthalimide.

a-Thiocyanoethylbenzene, $\text{CHMePh}\cdot\text{SCN}$, is a colourless oil and boils at $157-159^\circ$ under 36 mm. pressure.

Desyl thiocyanate, $\text{CHPhBz}\cdot\text{SCN}$, from bromodeoxybenzoin and potassium thiocyanate, crystallises from alcohol in colourless prisms and melts at $110-111^\circ$.

o-m-Xylyl thiocyanate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{SCN}$, is an oil which boils at 147° under 12 mm. pressure. *m*-Xylyl benzoyldithiocarbamate, $\text{NHBz}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}$, crystallises from alcohol in bright-yellow, needle-like prisms and melts at $93-94^\circ$. *Benzyl m*-xylyl benzoyl-*iminodithiocarbonate*, $\text{NBz}\cdot\text{C}(\text{S}\cdot\text{CH}_2\text{Ph})\cdot\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}$, prepared from benzyl benzoyldithiocarbamate and *m*-xylyl bromide, crystallises from alcohol and melts constantly at $97-98^\circ$; *m*-xylyl benzoyldithiocarbamate and benzyl chloride gave a compound melting at $85-89.5^\circ$, which seems to be an isomeric of the preceding compound, but did not melt like a pure substance.

m-Xylyl mercaptan, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{SH}$, is a colourless oil which boils at $215-217^\circ$ under atmospheric pressure. *Benzyl m*-xylyl sulphide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\text{Ph}$, is a colourless oil boiling at $193-196^\circ$ under 15 mm. pressure.

*Dirylyl benzoyl-*iminodithiocarbonate** crystallises from alcohol in colourless prisms and melts at $89.5-90^\circ$.

Mesityl thiocyanate, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CH}_2\cdot\text{SCN}$, crystallises from dilute alcohol in colourless plates and melts at 58° .

Mesityl benzoyldithiocarbamate, $\text{NHBz}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\text{Me}_2$, crystallises from alcohol in yellow plates or leaflets and melts at 114.5° .

*Benzyl mesityl benzoyl-*iminodithiocarbonate**, prepared from the preceding compound and benzyl chloride, or from benzyl benzoyldithiocarbamate and mesityl bromide, crystallises from alcohol in prisms, and melts at 117.5° .

T. M. L.

Nitrohydroxylaminic Acid. By FRANCESCO ANGELICO and S. FANARA (*Gazzetta*, 1901, 31, ii, 15-40).—The sodium salt of this acid can be obtained in a purer state than by Angeli's method (*Abstr.*, 1897, ii, 24) by replacing the ethyl nitrate by a methyl alcoholic solution of methyl nitrate. The potassium salt, $\text{K}_2\text{N}_4\text{O}_3$, forms a white, crystalline powder readily soluble in water. On treating solutions of the salts of nitrohydroxylaminic acid with silver nitrate, a voluminous yellow precipitate is obtained, rapidly changing to grey owing to separation of metallic silver, nitric oxide being at the same time evolved. The ammonium and hydrazine salts could not be prepared. The calcium ($3\frac{1}{2}\text{H}_2\text{O}$), strontium ($1\frac{1}{2}\text{H}_2\text{O}$), barium ($1\text{H}_2\text{O}$), cadmium ($1\text{H}_2\text{O}$), lead, and cerium [$\text{Ce}_2(\text{N}_2\text{O}_3)_2\cdot\text{Ce}(\text{OH})_5$] salts are described; they all decompose on heating, giving in some cases the metallic oxide and nitric oxide. With the sodium salt, however, the initial phase of the decomposition results in the formation of a mixture of nitrite and hyponitrite of sodium. If the decomposition of the salts is carried out in presence of aldehydes the :NOH group combines with

the aldehydes forming hydroxamic acids, the reaction taking place readily and in most cases giving theoretical yields.

Benzhydroxamic acid, $C_7H_7O_2N$, obtained by heating benzaldehyde with sodium nitrohydroxylamine and precipitating the acid in the form of its barium salt, crystallises from ether in white needles which melt and decompose at $129-131^\circ$. With copper acetate, it gives a pale green salt, and with ferric chloride an intense cherry-red coloration. When boiled with dilute sulphuric acid, it is resolved into benzoic acid and hydroxylamine; this reaction serves as a means of detection of small quantities of aldehydes.

Anishydroxamic acid, $C_8H_9O_3N$, prepared in a similar way, crystallises from acetone in sparkling scales melting and decomposing at 165° . With copper acetate, ferric chloride, and boiling dilute sulphuric acid, it behaves similarly to benzhydroxamic acid.

Piperonylhydroxamic acid, $C_9H_7O_4N$, separates from acetone in white crystals melting and decomposing at $172-173^\circ$, and gives the characteristic reactions of the hydroxamic acids.

The ethyl ether of salicylaldehyde gives the corresponding *hydroxamic acid*, $C_9H_{11}O_3N$, which separates from a mixture of benzene and ether in white needles melting at 139° . With ferric chloride and copper acetate, it gives the characteristic reactions.

Neither *o*-nitrobenzaldehyde nor nitropiperonaldehyde reacts with salts of nitrohydroxylaminic acid.

m-*Nitrobenzhydroxamic acid*, $C_7H_6O_4N_2$, separates from benzene in small, white crystals melting and decomposing at 153° .

Bromopiperonylhydroxamic acid, $C_8H_6O_4NBr$, is deposited from acetone in minute crystals melting and decomposing at 180° . It is slowly attacked when boiled with dilute sulphuric acid, yielding hydroxylamine and *bromopiperonylic acid* melting at 202° .

m-*Nitrosobenzhydroxamic acid* crystallises from ether in needles which melt and decompose at $73-76^\circ$ and are soluble in alkalis; at the ordinary temperature, it quickly decomposes, yielding a black resin and hence could not be analysed.

Hepthydroxamic acid, $C_7H_{15}O_2N$, crystallises from benzene in shining, white scales melting at $75-76^\circ$. When boiled with dilute sulphuric acid, this acid yields hydroxylamine and heptonic acid.

Formhydroxamic and acethydroxamic acids may be prepared by this method, and also the hydroxamic acids corresponding with propaldehyde, butaldehyde, and valeraldehyde.

Glyoxal yields a hydroxamic acid. *Suberyldihydroxamic acid* melts and decomposes at 135° and when boiled with dilute sulphuric acid yields suberic acid and hydroxylamine.

T. H. P.

Phenoxyacetic Anhydride. CHEMISCHE FABRIK AUF AKTIEN (SCHERING) (D.R.-P. 120772) — *Phenoxyacetic anhydride*,
 $O(CO \cdot CH_2 \cdot OPh)_2$,

prepared by heating sodium phenoxyacetate with phosphorus oxychloride dissolved in toluene, crystallises from ether in white, lustrous needles and melts at $67-69^\circ$; it dissolves in the ordinary organic solvents and is only slowly hydrolysed when boiled with water, in which it is insoluble.

G. T. M.

***o*-Toluoyl Chloride: Esters of Anthranilic Acid.** By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1901, 25, 793).—I. *o*-Toluoyl chloride boils at 209° and the corresponding cyanide at 221°; on hydrolysis, it yields *o*-toluoylformic acid, which when distilled is converted into *o*-toluic acid. *o*-Toluoylformamide melts at 130°. *ω*-Chloro-*o*-toluoyl chloride,



distils at 265°, but cannot be transformed into the corresponding cyanide.

II. Esters of anthranilic acid are best prepared by reducing the esters of nitrobenzoic acids with tin and hydrochloric acid. Only the methyl ester has a pleasant odour. The ester from fermentation amyl alcohol boils at 294° and has a feeble odour. *Methyl o*-nitrophenylacetate is a yellow liquid boiling at 264°. J. J. S.

Methyl Anthranilate. ERNST ERDMANN & HUGO ERDMANN (D.R.-P. 120120. Compare D.R.-P. 110386).—Methyl *o*-nitrobenzoate, produced by methylating *o*-nitrobenzoic acid with methyl alcohol and sulphuric acid, boils at 150.5° under 10 mm. pressure, has a sp. gr. 1.289 at 16°, and yields methyl anthranilate when reduced with stannous chloride, zinc dust or iron, and hydrochloric acid.

G. T. M.

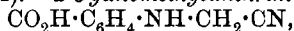
Alkyl Carboxyanthranilates from Phthalimide Derivatives containing Halogen Radicles attached to Nitrogen. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 119661).—Alkyl carboxyanthranilates, $\text{CO}_2\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\text{R}$, are readily prepared without the formation of bye-products by the action of dilute alcoholic solutions of sodium methoxide and ethoxide on phthalbromoimide or its chlorine analogue. The *dimethyl* ester, $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\text{Me}$, resulting from the employment of sodium methoxide in methyl alcohol, crystallises in needles, melts at 60–61°, and boils at 165–166° under 12 mm. pressure; it is readily soluble in the ordinary organic solvents. The corresponding *diethyl* ester melts at 43–44° and boils at 174° under 10 mm. pressure.

G. T. M.

Alkyl Acetylphenylglycine-*o*-carboxylates. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117059).—*Diethyl acetylphenylglycine-*o*-carboxylate* results from the action of acetyl chloride or anhydride on diethyl phenylglycine-*o*-carboxylate [or of alcoholic hydrogen chloride below 50° on acetylphenylglycine-*o*-carboxylic acid (Eng. Pat. 6628 of 1900)]; it forms lustrous crystals and melts at 62°. The *dimethyl* ester melts at 82–83°.

G. T. M.

***ω*-Cyanomethylantranilic Acid (Nitrile of Phenylglycine-*o*-carboxylic Acid).** FARBWERK MÜHLHEIM VORM. A. LEONHARDT & Co. (D.R.-P. 117924).—*ω*-Cyanomethylantranilic acid,



readily obtained by treating an alcoholic or aqueous solution of anthranilic acid hydrochloride in succession with potassium cyanide and formaldehyde, crystallises from water and melts at 184°; this compound is also formed on mixing the reagents in 50 per cent. acetic acid or in benzene.

G. T. M.

Phenylglycine-*o*-carboxylic Acid from Anthranilic Acid. FARBERWERK MÜHLHEIM VORM. A. LEONHARDT & Co. (D.R.-P. 120105).—*ω*-Cyanomethylantranilic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CN}$, prepared by adding formalin solution (1 mol. of formaldehyde) to an aqueous solution containing equivalent amounts of anthranilic acid hydrochloride, and potassium cyanide, separates as a white, voluminous precipitate soluble in alkalis and reprecipitated by acids; it crystallises from alcohol and melts at 184° .

The *amide* of phenylglycine-*o*-carboxylic acid is obtained on dissolving the nitrile in concentrated sulphuric acid, allowing the mixture to remain for 24 hours, and pouring the product on to ice; it crystallises from water and melts at 195° (compare Vorländer and Weissbrenner, Abstr., 1900, i, 295). The *thioamide* of the same acid results from the action of ammonia and yellow ammonium sulphide solution on the nitrile; it crystallises from water and melts at 190° . G. T. M.

Neutral Esters of Phenylglycine-*o*-carboxylic Acid. FARBERWERK MÜHLHEIM VORM. A. LEONHARDT & Co. (D.R.-P. 120138. Compare preceding abstract).—*ω*-Cyanomethylantranilic acid, when heated with an alcohol and a mineral acid, readily yields the corresponding neutral ester, $\text{CO}_2\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\text{R}$, of phenylglycine-*o*-carboxylic acid. The *methyl* ester melts at 93 – 94° and the *ethyl* ester at 75° . G. T. M.

Synthesis and Products of Dehydration of Unsaturated Acids. By MARUSSIA BAKUNIN (*Gazzetta*, 1901, 31, ii, 73–84).—In preparing unsaturated acids by the dehydration of aldehydes or of acids of the type $\text{CH}_2\text{R}\cdot\text{CO}_2\text{H}$ by means of acetic anhydride or acid, the author finds that the resinous secondary products always obtained are decreased in quantity if the reaction is carried out in a current of dry carbon dioxide. Thus the yield of benzylidenemalonic acid obtained from malonic acid, benzaldehyde, and acetic acid is greatly increased if the materials be heated in an atmosphere of carbon dioxide.

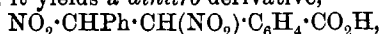
The formation of allo-isomerides (compare Abstr., 1897, ii, 622 and 623; this vol., i, 84) seems to take place first at high temperatures. Thus, by heating benzylidenemalonic acid at 195° , small quantities of *allocinnamic* acid are formed, whilst when the latter acid is heated with phosphoric oxide in chloroform solution it is apparently transformed, first into truxone, and on longer heating into indone. In the case of the ordinary cinnamic acid, heating with phosphoric oxide converts it into the anhydride, no truxone, but small quantities of a red substance melting at 170 – 180° , being obtained.

When benzaldehyde and sodium phenylacetate are heated together in a stream of carbon dioxide, phenylcinnamic acid is obtained in almost theoretical yield, together with small quantities of stilbene and of the allo-isomeride of the acid melting at 137° ; *aniline allophenylcinnamate*, $\text{C}_{15}\text{H}_{13}\text{O}_2\cdot\text{C}_6\text{H}_7\text{N}$, separates from benzene in long, silky needles melting at 128° . *allo*Phenylcinnamic acid, when boiled in chloroform solution with phosphoric oxide, appears to yield first the anhydride, then, on further heating, a red compound, phenylindone, which is gradually transformed into phenyltruxone.

The yield of phenyl-*o*-nitrocinnamic acid is increased if it is formed

in a current of carbon dioxide, but the formation of resinous products is not entirely prevented. In the preparation of phenyl *m*-nitrocinnamic acid, the allo-isomeride is also formed; the former acid, when heated with phosphoric oxide in chloroform solution, yields, firstly, the *anhydride*, $C_{30}H_{20}O_7N_2$, which is deposited from acetone in white needles, and, later, the corresponding substituted *indons* crystallising from benzene in bright red plates melting at 218° . Phenyl *p*-nitrocinnamic acid is obtained in almost theoretical yield when sodium phenylacetate and phenyl *p*-nitrobenzaldehyde are heated at 210° in carbon dioxide. If the temperature is 160° , a certain amount of the allo-isomeric acid is formed, which is, however, decomposed at 200° . T. H. P.

[Derivatives of] some Unsaturated Aromatic Acids. By ERNST LEUPOLD (*Ber.*, 1901, 34, 2829—2837).—*Ammonium stilbene-o-carboxylate*, with H_2O , crystallises in lustrous prisms and the *silver salt* in a silvery, fan-shaped mass of crystals. When the acid is treated with nitrous acid, it yields a *dinitro-derivative*,

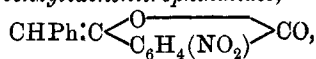


which is a greenish, crystalline substance melting and decomposing at 123° , and, when boiled with acetic acid, forms nitrobenzalphthalide. The *dibromide* of stilbene-*o*-carboxylic acid is a white, crystalline substance which melts and decomposes at 180° ; when boiled with acetic acid, it yields the *lactone*, $C_6H_4 \cdot \begin{smallmatrix} CHBr \cdot CHPh \\ \diagdown \quad \diagup \\ CO \quad \quad O \end{smallmatrix}$, which crystallises in

silvery needles melting at 137° . When warmed with concentrated sulphuric acid, the acid yields the *lactone*, $C_6H_4 \cdot \begin{smallmatrix} CH_2 \cdot CHPh \\ \diagdown \quad \diagup \\ CO \quad \quad O \end{smallmatrix}$, which crystallises in slender needles and melts at 89° .

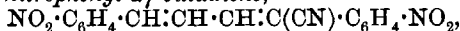
The *dibromide* of *o*-carboxycinnamic acid crystallises in small, colourless columns, melts at 189° , and when warmed with acetic acid yields phthalylacetic acid. *o*-Carboxycinnamic acid, when warmed with concentrated sulphuric acid, yields a lactonic acid, $C_{10}H_8O_4$ (either dihydroisocoumarincarboxylic acid or the lactone of α -benzylhydril-acetic acid), which forms a *barium salt* crystallising with $4H_2O$, a *silver salt* crystallising in silky needles, and an *ethyl ester* crystallising in slender needles.

A mixture of two *benzylidenenitrophthalides*,



melting respectively at 277° and $232-233^\circ$, was obtained by the condensation of 4-nitrophthalic anhydride and phenylacetic acid. *p*-Nitrophenylacetic acid and phthalic anhydride condense, forming *m*-nitrobenzylidenephthalide, $NO_2 \cdot C_6H_4 \cdot CH : C \begin{smallmatrix} \diagup O \diagdown \\ \diagdown C_6H_4 \diagup \end{smallmatrix} CO$, which crystallises in brownish-yellow needles melting at 222° . R. H. P.

Formation of Substantive Azo-dyes from Di-*p*-aminophenylcyanobutadiene. By MARTIN FREUND (*Ber.*, 1901, 34, 3109).—*p*-Nitrocinnamaldehyde and *p*-nitrobenzyl cyanide condense, forming *α*-cyano- α -di-*p*-nitrophenyl- γ -butadiene,



which crystallises in small, yellow needles and melts at 276° ; the

corresponding *amino*-compound forms brownish-yellow crystals, melts at 196°, and yields substantive azo-dyes. R. H. P.

Synthesis of Tertiary Aromatic Acids. By AUGUSTIN BISTRZYCKI and K. WEHRBEIN (*Ber.*, 1901, **34**, 3079—3081. Compare this vol., i, 701, 716).—*Diphenyl-p-tolylacetic acid*, $C_6H_4Me \cdot CPh_2 \cdot CO_2H$, and its homologues are readily prepared by condensing benzoic acid with toluene and other aromatic hydrocarbons in the presence of tin tetrachloride. This compound crystallises from dilute alcohol in spherical aggregates of colourless plates melting at 205°; its *silver* salt, $C_{21}H_{17}O_2Ag$, is a white, insoluble substance. G. T. M.

Benzyl Salicylate. AKTIEN-GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P. 119463).—*Benzyl salicylate*, $OH \cdot C_6H_4 \cdot CO_2 \cdot CH_2Ph$, prepared by heating anhydrous potassium salicylate with benzyl chloride at 130—140° for 14 hours, is a colourless, odourless liquid boiling at 208° under 26 mm. pressure; it is scarcely soluble in water, but dissolves more readily in ether or alcohol. It yields sparingly soluble salts with the alkali hydroxides, and is hydrolysed into its generators by alcoholic potassium hydroxide solution. G. T. M.

New Crystallised Bismuth Salicylate. By PAUL THIBAUT (*Bull. Soc. Chim.*, 1901, [iii], **25**, 794—796).—The action of salicylic acid on hydrated bismuth oxide does not result in the formation of any pure compound, but if the yellow, crystalline anhydrous oxide, obtained by boiling bismuth nitrate solution with excess of alkali hydroxide, is employed, *bismuth salicylate*, $Bi_2O_3(C_7H_6O_3)_3$, is readily produced. It crystallises in small, anisotropic prisms melting and decomposing at 100°, is not acted on by cold alcohol or ether, and is slowly decomposed by cold, more quickly by hot, water. N. L.

Disalicylide. By ALFRED EINHORN and HERMANN PFEIFFER (*Ber.*, 1901, **34**, 2951—2953. Compare Anschütz, *Abstr.*, 1893, i, 165).—

Disalicylide, $C_6H_4 \begin{smallmatrix} O \cdot CO \\ CO \cdot O \end{smallmatrix} C_6H_4$, is formed when carbonyl chloride is passed into an ice-cold solution of salicylic acid in pyridine, the operation lasting from 1 to 1.5 hours; the mixture is kept for several days, and then poured into ice-cold, extremely dilute sulphuric acid. It crystallises from acetic acid or chloroform in prismatic needles melting at 200—201°. It may be distilled without decomposition, is not decomposed by sodium hydroxide or carbonate solutions, and when heated with phenol for several hours at 200° yields salol.

Other *o*-hydroxy-acids may be converted into dianhydrides by similar methods.

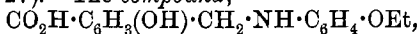
o-*Dicresotide* melts at 213.5°, the meta-compound at 207.5°, and the para-isomeride at 243.5°. The bimolecular *anhydride* of mandelic acid melts at 240°, of benzoic acid at 196°, and of *α*-hydroxyisobutyric acid at 27.78°. J. J. S.

Condensation Products of the Haloid Derivatives of Hydroxytolualdehyde and Hydroxytoluic Acid with the Phenols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117890).—*p*-Chloromethylsalicylic acid and *β*-naphthol, when boiled with glacial acetic

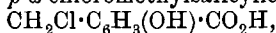
acid, yield a crystalline compound, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_{10}\text{H}_7$, melting at 198° ; the corresponding products from phenol, *o*-cresol, and thymol melt at 159° , 226° , and 250° respectively. The *isobutyl-o*-cresol, resorcinol, pyrogallol, and guaiacol compounds melt at 177° , 249° , 243° , and 210° respectively. *p*- ω -Chloromethylsalicylaldehyde reacts in a similar manner (compare D.R.-P. 114194). G. T. M.

Acetyltropic Acid. By OSWALD HESSE (*J. pr. Chem.* 1901, [ii], 64, 286—288).—Under the influence of acetic anhydride or acetyl chloride, tropic acid in combination with alkaloids (of *Solanaceae*) is readily converted into atropic acid. When warmed with acetic anhydride, tropic acid yields *acetyltropic acid*, $\text{OAc}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, which forms flattened crystals melting at 80° . On boiling a solution of the acetyl derivative in potassium hydroxide, hydrolysis takes place, but atropic and not tropic acid is produced. K. J. P. O.

Preparation of Condensation Products from Substituted Hydroxybenzyl Haloids and Amines. FARBENFABRIKEN VORM. F. BAYER & Co (D.R.-P. 121051. Compare D.R.-P. 113723 and 114194, and this vol., i, 727).—The compound,



prepared by condensing *p*- ω -chloromethylsalicylic acid,



and phenetidine in ethereal solution, crystallises in yellow needles and melts at 161° . This hydroxy-acid and dimethylamine give rise to the compound $\text{NMe}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$, a substance crystallising in colourless needles and melting at 216° .

p-Chloromethylsalicylaldehyde and piperidine yield the compound $\text{CHO}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}$, which forms a brownish-white, amorphous powder.

Methyl *o*-chloromethyl-*p*-hydroxybenzoate, $\text{CH}_2\text{Cl}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{Me}$, and dimethylamine yield the *methyl ester*, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{Me}$, melting at 83° ; the corresponding *ethyl ester* melts at 62° . G. T. M.

Preparation of *p*-Aminophenylglyoxylic Acid and its Homologues, and Substitution Products. C. F. BOEHRINGER & SONS (D.R.-P. 117021. Compare Abstr., 1874, 421, and D.R.-P. 112174).—*p*-Aminophenylglyoxylic acid and its homologues and substitution products are readily obtained by oxidising *p*-aminophenyltartronic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{CO}_2\text{H})_2\cdot\text{OH}$, and its derivatives with manganese dioxide (Weldon mud), mercuric oxide, ferric chloride, potassium permanganate, or arsenious acid, in acid or in alkaline solution. *p*-Aminophenylglyoxylic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$, obtained from the potassium hydrogen salt of the corresponding tartronic acid, crystallises in yellow needles or lamellae, and sinters at 190° ; its *phenylhydrazone* crystallises in yellow needles and melts at 163 — 164° .

p-Methylaminophenylglyoxylic acid crystallises from water in orange-yellow prisms and melts at 155 — 157° ; the phenylhydrazone melts at 166° . The corresponding *ethyl derivative* melts at 116° . *Diethylaminophenylglyoxylic acid*, $\text{NEt}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$, crystallises in yellow prisms and melts at 114 — 116° ; the corresponding dimethyl compound (Abstr., *loc. cit.*) furnishes a phenylhydrazone sintering at

175° and melting at 181°. *Ethylene-p-diaminodiphenylglyoxylic acid*, $C_2H_4 \cdot N_2H_2(C_6H_4 \cdot CO \cdot CO_2H)_2$, melts and decomposes at 205—208°. *p-Aminomethoxyphenylglyoxylic acid*, $NH_2 \cdot C_6H_3(OMe) \cdot CO \cdot CO_2H$, melts at 147—148°. The compound, $NHPh \cdot C_6H_4 \cdot CO \cdot CO_2H$, is tarry, but yields a *phenylhydrazone* melting at 168°. *Benzylmethylaminophenylglyoxylic acid*, $C_7H_7 \cdot NMe \cdot C_6H_4 \cdot CO \cdot CO_2H$, melts at 85—87°.

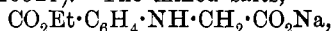
p-Amino-m-tolylglyoxylic acid, $NH_2 \cdot C_7H_6 \cdot CO \cdot CO_2H$, prepared from *p-amino-m-tolyltartronic acid*, crystallises in needles melting at 163—164°; the *phenylhydrazone* melts at 179°.

p-Ethylamino-m-tolylglyoxylic acid, $NHEt \cdot C_7H_6 \cdot CO \cdot CO_2H$, forms yellow needles and melts at 132—134°. G. T. M.

p-Aminophenylglyoxylic Acid and its Derivatives. C. F. BOEHRINGER & SONS (D.R.-P. 117168).—The condensation product of alloxan with an aromatic base (compare Pellizzari, Abstr., 1888, 142; also D.R.-P. 112174) is readily converted into the corresponding aminophenylglyoxylic acid by successive oxidation and hydrolysis, without isolation of the intermediate tartronic acid (compare preceding abstract).

p-Methylanilalloxan yields *p-methylaminophenylglyoxylic acid* when treated with mercuric oxide and sodium hydroxide. The acid $C_{11}H_{12}O_3N_2$, obtained from dimethylanilalloxan by the action of a 10 per cent. alkali solution, furnishes *p*-dimethylaminophenylglyoxylic acid when treated with manganese dioxide and sodium hydroxide. *p-Amino-m-tolylglyoxylic acid*, *p-methylbenzylaminophenylglyoxylic acid*, and *p*-dimethylaminobenzoylformic acid are also obtained by similar means from the corresponding alloxan derivatives. G. T. M.

Preparation of Indigo and its Derivatives from the Esters of Phenylglycine-*o*-carboxylic Acid. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 120321).—The mixed salts,



and $CO_2Na \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO_2Et$, when treated in succession with acetic anhydride, sodium hydroxide, and atmospheric oxygen, yield indigo. The salt, $CO_2Me \cdot C_6H_3Cl \cdot NH \cdot CH_2 \cdot CO_2H$, derived from *o*-nitro-*m*-chlorobenzoic acid under these conditions gives rise to dichloro-indigo. G. T. M.

Preparation of Indigotin and its N-Alkyl Derivatives. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 120900).—An intimate mixture of sodium *o*-chlorobenzoate, glycine, and potassium or sodium hydroxide heated for some time at 150—250°, and subsequently dissolved in water saturated with carbon dioxide, yields indigotin on oxidation. When the glycine is replaced by its methyl or ethyl derivative, the corresponding N-alkylindigotins are produced. G. T. M.

Molecular Weight of Indigo-blue and of Indigo-red. By WILHELM VAUBEL (*Chem. Zeit.*, 1901, 25, 725—726. Compare Sommaruga, Abstr., 1879, 63, 532).—The molecular weights of indigotin and indigo-red have been determined by the cryoscopic method in various solvents. Indigotin in *p*-toluidine or phenol gives results that

point to the double molecular formula $C_{22}H_{20}O_4N_4$, but in aniline solution to the simple formula $C_{16}H_{10}O_2N_2$. Indigo-red in *p*-toluidine solution also appears to have the higher molecular weight, namely, 524.
J. J. S.

Condensation of Indigo-white with Formaldehyde. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 120318).—Indigo-white, when treated with formaldehyde in neutral aqueous or alcoholic solutions, yields an insoluble compound which separates as a green powder. The product is sparingly soluble in water, cold alcohol, ether, or the aromatic hydrocarbons, but dissolves more readily in acetone, glacial acetic acid, or hot alcohol; from the last of these, it separates in greenish-yellow leaflets melting at 215° , and gradually changes into indigo. It is readily decomposed into its generators by alkali carbonates or hydroxides at the ordinary temperature, and a similar hydrolysis occurs when it is boiled with water.
G. T. M.

New Hydro-compound of Indigotin and its Application to Quantitative Estimation. By WILHELM VAUBEL (*Zeit. angew. Chem.*, 1901, 14, 892—893).—When indigo is shaken with an alcoholic solution of potassium hydroxide of appropriate concentration and zinc dust, the dye rapidly dissolves, forming a deep-red solution. Excess of zinc dust finally bleaches this solution, with the production of indigo-white, whilst the access of air regenerates indigotin. Other reducing agents, as iron, ferrous sulphate, aluminium, &c., also bring about this phenomenon. The author expresses the opinion that there is formed an intermediate product, "dihydroindigotin," between indigotin and indigo-white, and suggests that its production may be used as a basis for a colorimetric estimation of commercial indigos.

K. J. P. O.

β -Naphthoxyacetic Acid and its Derivatives. By FRITZ SPITZER (*Ber.*, 1901, 34, 3191—3205).—Details are given for the preparation of β -naphthoxyacetic acid from β -naphthol and chloroacetic acid. The pure substance melts at 156° , not at 151 — 152° as given by Spica (*Abstr.*, 1887, 495), and is not sensitive to light. It is best nitrated in glacial acetic acid solution, and not by the method of the German Patent 58614; the product is 1-nitro-2-naphthoxyacetic acid, which crystallises from the solvent in yellow needles, melts at 192° , and is not hydrolysed by acids or alkalis under pressure. An attempt to synthesise the nitro-compound from 1-nitro- β -naphthol and chloroacetic acid gave only a resinous product, but its structure follows from that of the derived aminonaphthoxyacetic acid (*infra*); the ammonium salt forms lustrous, yellow, rhombic plates, the potassium salt crystallises with $\frac{1}{2}H_2O$, and the sodium salt with $1H_2O$ in lustrous, yellow needles; the ethyl ester crystallises in lustrous, slightly yellow needles and melts at 100° , and the chloride in yellow plates melting at 94° ; the amide and anilide separate from alcohol in needles and melt respectively at 189° and 139° .

1-Amino-2-naphthoxyacetic anhydride, $C_{10}H_6 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CH}_2 \end{smallmatrix}$, obtained by

the reduction of the nitro-compound with stannous chloride and hydrochloric acid, crystallises from alcohol in white, lustrous needles and melts at 217° ; it is not soluble in alkali carbonates, but yields crystalline salts with alkali hydroxides. It is not esterified by alcohol and hydrogen chloride, and cannot be hydrolysed.

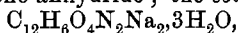
1-Acetyl-amino-2-naphthoxyacetic acid, obtained by condensing 1-acetyl-amino- α -naphthol with chloroacetic acid by means of potassium hydroxide, separates from water in leaflets, melts at $234-235^{\circ}$, and yields an *ethyl* ester crystallising from alcohol in white needles and melting at 128° ; the hydrolysis of the acetyl derivative by alkalis yields the foregoing 1-amino-2-naphthoxyacetic acid, thus proving the structure of the latter.

Trinitro-2-naphthoxyacetic acid, obtained by the nitration of the mononitro-compound dissolved in concentrated sulphuric acid, crystallises from alcohol in yellowish-white needles and melts and decomposes at $239-240^{\circ}$; the *ammonium* salt (anhydrous), the *potassium*-salt, with $1\text{H}_2\text{O}$, and the *sodium* salt, with $\frac{1}{2}\text{H}_2\text{O}$, form small, yellow needles. The *ethyl* ester crystallises from glacial acetic acid in small, feebly-yellow needles or lustrous leaflets, and melts and decomposes at $227-228^{\circ}$. The *chloride*, *amide*, and *anilide* form small, yellow plates or needles and melt and decompose at $159-160^{\circ}$, $221-222^{\circ}$, and $232-233^{\circ}$ respectively.

All attempts to diazotise 1-amino-2-naphthoxyacetic anhydride failed, but on warming with acetic acid and sodium nitrite solution it was converted into 4-nitro-1-amino-2-naphthoxyacetic anhydride,

$\text{NO}_2 \cdot \text{C}_{10}\text{H}_5 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \diagdown \quad \diagup \\ \text{O} - \text{CH}_2 \end{smallmatrix}$, which crystallises in yellow needles and leaflets,

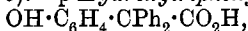
commences to decompose at about 290° , and is also obtained by the action of nitric acid on the anhydride; the *sodium* salt,



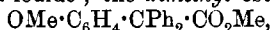
crystallises in yellow needles and is decomposed by dilute hydrochloric acid to form a red *sodium hydrogen* salt; the *potassium hydrogen* salt, $\text{C}_{12}\text{H}_7\text{O}_4\text{N}_2\text{K} \cdot 1\frac{1}{2}\text{H}_2\text{O}$, crystallises in reddish-yellow needles.

W. A. D.

Condensation of Benzilic Acid with Phenols. By AUGUSTIN BISTRZYCKI and LEON NOWAKOWSKI (*Ber.*, 1901, **34**, 3063—3073. Compare Abstr., 1897, i, 190).—*p-Hydroxytriphenylacetic acid*,

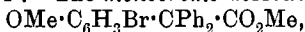


prepared by condensing benzilic acid with phenol in the presence of tin tetrachloride, crystallises from dilute alcohol in colourless or pale yellow leaflets melting at 212° , and is readily soluble in all the ordinary organic solvents excepting light petroleum. The *silver* salt is a white, insoluble substance; the other metallic derivatives could not be obtained crystalline. The silver salt does not yield an ester on treatment with methyl iodide; the *dimethyl* ester,



is formed, however, on heating a mixture of the acid, methyl iodide, methyl alcohol, and potassium hydroxide at 100° ; it crystallises from glacial acetic acid, and melts at $138-139^{\circ}$. This ethereal salt is insoluble in cold dilute potassium hydroxide solution, and is hydrolysed

with great difficulty when heated at 100° with this alkali dissolved in methyl alcohol. *p*-Methoxytriphenylacetic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$, the product of this hydrolysis, crystallises from dilute acetic acid in needles melting at 174° . The monobromo-derivative,

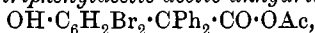


resulting from the action of bromine on the dimethyl ester, crystallises in pale yellow prisms and melts at 126° .

p-Acetoxytriphenylacetyl acetate, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{CO}_2\text{Ac}$, crystallises in needles melting at 208° ; it is not soluble in cold dilute sodium hydroxide solution, but is hydrolysed by a hot concentrated solution of this reagent.

Dibromo-p-hydroxytriphenylacetic acid, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$, produced by brominating the free acid in glacial acetic acid, crystallises in colourless needles and melts at $194\text{--}195^{\circ}$.

Dibromo-p-hydroxytriphenylacetic acetic anhydride,

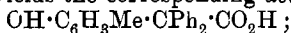


formed by the action of acetic anhydride on the preceding compound, crystallises in white needles melting at $212\text{--}213^{\circ}$; it is insoluble in cold dilute solutions of the alkalis.

Nitro p-hydroxytriphenylacetic acid, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$, obtained by nitrating the acid in glacial acetic acid, crystallises from this solvent in yellow needles melting at $177\text{--}178^{\circ}$.

m-Tolyldiphenylacetic acid lactone, $\text{CO}\langle\text{O}\rangle_{\text{CPh}_2}\text{C}_6\text{H}_3\text{Me}$, prepared by

condensing benzilic acid and *m*-cresol with tin tetrachloride, crystallises in lustrous, snow-white needles melting at 126° ; it is insoluble in dilute sodium hydroxide solution, but on boiling with concentrated solutions of the alkali hydroxides it becomes hydrolysed and the product, when acidified, yields the corresponding acid,



this substance has not, however, been obtained pure, owing to the readiness with which it passes back into the lactone. *Bromo-m-tolyldiphenylacetic acid lactone*, $\text{CO}\langle\text{O}\rangle_{\text{CPh}_2}\text{C}_6\text{H}_2\text{MeBr}$, crystallises in

colourless plates and melts at $158\text{--}159^{\circ}$.

p-Hydroxy-*m*-tolyldiphenylacetic acid (*4*-hydroxy-2-methyltriphenylacetic acid), $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$, produced as a bye-product in the preceding condensation, crystallises in colourless needles and melts at $212\text{--}213^{\circ}$; its diacetyl derivative, $\text{OAc}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CPh}_2\cdot\text{CO}\cdot\text{OAc}$, crystallises in aggregates of colourless plates melting at 189° .

p-Tolyldiphenylacetic acid lactone, resulting from the condensation of benzilic acid and *p*-cresol, crystallises from alcohol in lustrous, pale yellow prisms melting at 130° ; the acid is extremely unstable and could not be isolated in a state of purity. The bromo-derivative,

$\text{CO}\langle\text{O}\rangle_{\text{CPh}_2}\text{C}_6\text{H}_2\text{MeBr}$, melts at 161° .

p-Hydroxy-*o*-tolyldiphenylacetic acid, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$, prepared from benzilic acid and *o*-cresol, crystallises in colourless plates and melts at 190° ; the silver salt is unstable, whilst the green precipitate, produced by adding copper acetate to a solution of the potassium salt, has the composition of a basic salt. G. T. M.

Artemisin. By P. BERTOLO (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 111—116. Compare Merck, *Abstr.*, 1896, i, 59).—Artemisin forms with chloroform a crystalline compound of the composition $C_{15}H_{18}O_4 \cdot CHCl_3$, the formation of which serves as a convenient means of obtaining pure artemisin, since the whole of the chloroform is evolved at 80° .

The sodium salt of artemisin, obtained by treating an aqueous alcoholic solution of artemisin with sodium carbonate, crystallises from alcohol in shining, colourless, flattened needles which effloresce when kept over sulphuric acid; it is very soluble in water, the solution having a bitter, saline taste. Treated with dilute sulphuric acid, it yields artemisin, whilst treatment with concentrated sulphuric acid gives a white precipitate which separates from alcohol in large, tabular crystals melting at 170 — 171° ; this substance is to be further investigated. The silver salt of artemisin, $C_{15}H_{19}O_5Ag$, separates as a white precipitate.

Artemisin oxime, $C_{15}H_{19}O_4N$, crystallises from methyl alcohol in white, silky needles, which sometimes form star-shaped aggregates and melt at 233 — 234° ; it is slightly soluble in water, readily in alcohol, ether, or chloroform, and dissolves also in cold dilute aqueous alkali hydroxides.

Artemisin apparently forms a hydrazone and an osazone.

T. H. P.

Behaviour of Bromine towards the Unsaturated Condensation Products from Benzyl Cyanide and the Substituted Benzaldehydes. By AUGUSTIN BISTRZYCKI and ERWIN STELLING (*Ber.*, 1901, 34, 3081—3089. Compare Frost, *Abstr.*, 1889, 597, and Walther and Wetzlich, *Abstr.*, 1900, i, 438).— *α -Phenylbromopiperonylcinnamitrile*, $C_7H_4O_2Br \cdot CH : CPh \cdot CN$, produced by brominating the condensation product of piperonaldehyde and benzyl cyanide in chloroform solution, crystallises in yellow prisms and melts at 179° . *α -Phenyl-p-hydroxycinnamitrile*, $OH \cdot C_6H_4 \cdot CH : CPh \cdot CN$, obtained by condensing p-hydroxybenzaldehyde and benzyl cyanide in an absolute alcoholic solution of sodium ethoxide, crystallises from dilute alcohol in colourless needles melting at 192° ; it does not form an additive compound with bromine. A stereoisomeric substance is formed when the reaction is repeated in dilute alcohol; this compound also melts at 190 — 191° , but differs from its isomeride in being insoluble in chloroform, carbon disulphide, or benzene, whereas the preceding compound is soluble in the organic solvents, excepting light petroleum. The acetyl derivative, $OAc \cdot C_6H_4 \cdot CH : CPh \cdot CN$, forms colourless leaflets and melts at 121 — 122° .

m-Hydroxybenzaldehyde and benzyl cyanide yield the same product whether they are condensed with sodium ethoxide or hydroxide; this compound, *α -phenyl-m-hydroxycinnamitrile*, crystallises from dilute acetic acid in plates melting at 106 — 107° ; its acetyl derivative melts at 75 — 76° .

The dibromide, $C_{15}H_9ONBr_2$, produced in chloroform solution, crystallises in prisms and melts at 182° ; this reaction does not take place very readily and the yield of additive product is very small. Vanillin

and salicylaldehyde do not interact with benzyl cyanide, whilst cumin-aldehyde gives rise to tarry products.

α-Phenyl-m-ethoxycinnamonitrile, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CPh} \cdot \text{CN}$, prepared from *m*-ethoxybenzaldehyde, crystallises from alcohol in aggregated plates and melts at 72° ; the *dibromide*, $\text{C}_{17}\text{H}_{13}\text{ONBr}_2$, forms lustrous leaflets or white, felted needles and melts at 119° ; its formation is accompanied by a considerable evolution of hydrogen bromide and it is probably a substitution product having one or other of the formulæ $\text{OEt} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH} : \text{CPh} \cdot \text{CN}$ or $\text{OEt} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CBr} : \text{CPh} \cdot \text{CN}$.

α-Phenyl-o-ethoxycinnamonitrile, obtained from the ethyl derivative of salicylaldehyde, crystallises in snow-white needles and melts at 82° . The *tribromide*, $\text{OEt} \cdot \text{C}_6\text{H}_4\text{Br} \cdot \text{CHBr} \cdot \text{CBrPh} \cdot \text{CN}$, produced from the preceding nitrile and 6 atomic proportions of bromine, crystallises in plates melting at 114° with a liberation of bromine; this behaviour seems to indicate that the substance is a dibromide.

α-Phenyl-p-methoxydibromocinnamonitrile, $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH} : \text{CPh} \cdot \text{CN}$, results from the action of bromine (6 atoms.) on *α-phenyl-p-methoxycinnamonitrile*, the action being attended by the liberation of hydrogen bromide; it forms prismatic lamellæ and melts at 186° ; the bromine is not removed by heating with sodium ethoxide.

α-Phenyl-m-bromo-p-methoxycinnamonitrile, prepared by condensing *m*-bromoanisaldehyde and benzyl cyanide, crystallises in silky prisms and melts at 102° .

α-Phenyl-p-methylcinnamonitrile, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH} : \text{CPh} \cdot \text{CN}$, derived from *p*-tolylaldehyde, crystallises from alcohol either in rhombic or monoclinic prisms, both forms melting at 61° ; it absorbs bromine very slowly, yielding tarry products. G. T. M.

Constitution of Dibromophthalic Acid. By O. BRÜCK (*Ber.*, 1901, **34**, 2741—2747).—The dibromophthalic acid described by Juvalta (*D.R.-P.* 50177) and by Blümlein (*Abstr.*, 1885, 162) is shown by two separate methods to be 4:5-dibromo-1:2-phthalic acid.

Dimethyl 4:5-dibromophthalate, $\text{C}_6\text{H}_2\text{Br}_2(\text{CO}_2\text{Me})_2$, crystallises from methyl alcohol in colourless needles and melts at 81 — 83° . The *diethyl ester*, $\text{C}_{12}\text{H}_{12}\text{O}_4\text{Br}_2$, crystallises from alcohol in glistening, transparent needles and melts at 63 — 65° . The *monoethyl ester*, prepared by heating the anhydride with absolute alcohol, forms long needles, melts at 147 — 149° , and can also be prepared by hydrolysing the diethyl ester with alcoholic potassium hydroxide. The formation of these esters corresponds with the behaviour of a 4:5-acid, but not with that of a 3:4- or 4:6-acid.

By fusing with potassium hydroxide, the acid is converted into a dihydroxyphthalic acid identical with the 4:5-acid described by Rossin (*Abstr.*, 1892, 180) and by Freund (*Abstr.*, 1893, i, 117); the acid, contrary to the description of Rossin and Freund, was observed to melt with formation of the anhydride at 175° , but the identity of the two acids was proved by crystallographic measurements and the constitution of the dibromo-acid was thus established.

4:5-Dibromophthalimidine, $\text{C}_6\text{H}_2\text{Br}_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{>NH}$, prepared by re-

ducing the phthalimide with tin and hydrochloric acid, crystallises from alcohol in glistening, white needles with a greenish shimmer, melts at $279-280^{\circ}$ to a turbid red liquid, and has no marked basic properties. The nitroso-derivative, $C_6H_2Br_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{NO}$, crystallises from alcohol in yellow needles, melts at $183-185^{\circ}$ to a turbid liquid, and gives Liebermann's reaction. 4:5-Dibromophthalide, $C_6H_2Br_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{O}$, prepared by the action of sodium hydroxide on the nitroso-derivative, sublimes in pure white crystals and melts at $225-227^{\circ}$; it is reduced by phosphorus and hydriodic acid to the 4:5-dibromo-*o*-toluic acid described by Claus and Beck (Abstr., 1892, 1207), thus again establishing the constitution of the dibromophthalic acid.

T. M. L.

Action of Sulphuryl Chloride on Methyl Protocatechuate. Dichloroprotocatechuic Acid and Dichloroveratric Acid. By GIROLAMO MAZZARA (*Gazzetta*, 1901, 31, i, 554-560; ii, 94-104).—The action of sulphuryl chloride on methyl protocatechuate (methyl 3:4-dihydroxybenzoate), gives rise to two isomeric methyl dichloroprotocatechuates, $C_6HCl_2(OH)_2 \cdot CO_2Me$, the relations between which are not yet definitely established. One ester crystallises from dilute alcohol in almost white needles having a pale rose tint and melting with slight decomposition at $223-225^{\circ}$; it dissolves slightly in water, the solution giving with ferric salts a chrome-green coloration whilst solutions of the alkali carbonates dissolve the ester with formation of a yellowish-green colour. The other ester crystallises from dilute alcohol in long, slender, sparkling needles containing $1H_2O$, whilst when dried it separates from benzene in white needles melting at 105° ; in aqueous solution, it yields an indigo-blue coloration with ferric chloride.

The two methyl dichloroprotocatechuates (*loc. cit.*) form, with ammonium salts, precipitates which are readily decomposed by sodium carbonate solutions and the examination of which is being continued.

Since the two dichloroprotocatechuic acids obtained by hydrolysing the two methyl esters are readily and almost quantitatively esterified by means of alcohol and hydrogen chloride, these esters must have the constitutions $CO_2Me : Cl_2 : (OH)_2 = 1 : 2 : 5 : 3 : 4$ or $1 : 5 : 6 : 3 : 4$; the ester melting at 105° , which crystallises with $1H_2O$, probably has the first of these constitutions.

Dichloroprotocatechuic acid, $C_6HCl_2(OH)_2 \cdot CO_2H, 3H_2O$, obtained by hydrolysing the methyl ester melting at 105° , crystallises from aqueous alcohol in long, silky prisms; in aqueous solution, it gives a blue coloration with ferric chloride. The isomeride prepared from the methyl ester melting at $223-225^{\circ}$ separates from alcohol in sparkling prisms which blacken slightly at 230° and melt and decompose at 239° ; its aqueous solution gives an azure-blue coloration with ferric salts.

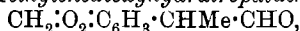
Methyl dichloroveratrate, $C_6HCl_2(OMe)_2 \cdot CO_2Me$, prepared from the dichloroprotocatechuic acid melting at 239° by heating it with potassium hydroxide and methyl iodide in presence of methyl alcohol, crystallises from aqueous alcohol in small prisms melting at $95-96^{\circ}$.

The corresponding *dichloroveratric acid* is deposited from dilute alcohol in small crystals, which, after drying at 100°, melt at 182—183°; it is slightly soluble in water, its solution giving no coloration with ferric salts, and on esterification the methyl ester is obtained in almost quantitative proportion. T. H. P.

***p*-Methoxyatrolactic Acid.** By J. BOUGAULT (*Bull. Soc. Chim.*, 1901, [iii], 25, 854—856).—*p*-Methoxyatrolactic acid,
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{H}$,

best obtained by the oxidation of *p*-methoxyhydratropic acid (Abstr., 1901, i, 548) in the cold with a large excess of potassium permanganate, is a crystalline substance melting at 129—130° and is optically active. The action of hydriodic acid converts it into *p*-hydroxyhydratropic acid. The sodium and calcium salts crystallise with 2H₂O. N. L.

3 : 4-Dioxymethylenehydratropic Aldehyde and Acid. By J. BOUGAULT (*Bull. Soc. Chim.*, 1901, [iii], 25, 856—858. Compare Abstr., 1900, i, 495).—3 : 4-Methylenedioxyhydratropaldehyde,



obtained by oxidising *isosafrole* in ethereal solution with a mixture of mercuric oxide and iodine, is a colourless, highly refracting liquid which boils at 279—280°, and has a sp. gr. 1.203 at 15°; the *oxime* melts at 71°. Chromic acid oxidises the aldehyde to 3 : 4-methylenedioxyacetophenone, whilst potassium permanganate in alkaline solution converts it into 3 : 4-methylenedioxyphenylglyoxylic acid and finally into piperonic acid.

3 : 4-Methylenedioxyhydratropic acid, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CHMe}\cdot\text{CO}_2\text{H}$, obtained by oxidising the corresponding aldehyde with silver oxide in alkaline solution, forms anhydrous, prismatic crystals melting at 80°. Chromic acid oxidises it to the ketone, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:COMe}$, and potassium permanganate to piperonic acid. By repeated crystallisation of its morphine salt, the acid may be resolved into two optically active components. The sodium, calcium (with 2H₂O), copper, and silver salts have been prepared. N. L.

Naphthalic Acid and Naphthalimide. By LUIGI FRANCESCONI and V. RECCHI (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 85—93).—In order to follow up the analogies observed in the behaviour of phthalic and 1 : 8-naphthalic acid, the authors have studied the reactions of the latter acid with antimony pentachloride and of the amide of this acid with alkali hypobromite and hypochlorite.

By heating 1 : 8-naphthalic anhydride with antimony pentachloride at 180° and afterwards passing chlorine into the mixture, two compounds are obtained: (1) *Hexachloronaphthalic anhydride*, C₁₂O₃Cl₆, which crystallises from acetic acid in lustrous, pale yellow plates melting at 205°; it is soluble in ethyl acetate or acetone, and slightly so in alcohol. With resorcinol, it condenses, giving a fluorescent solution which is green by reflected, and yellowish-red by transmitted light. Sulphuric acid does not give the azure fluorescence which it does with tetrachlorophthalic anhydride. It is slightly soluble in concentrated sodium carbonate solution, from which mineral acids precipitate *hexachloronaphthalic acid* in the form of white flocks; this, when boiled with alcohol, is reconverted into the anhydride. (2) A carbon chloride

of the composition $C_{12}Cl_{14}$, which, when slowly deposited from ether, is obtained in crystals resembling cubes, whilst rapid crystallisation yields acicular crystals; from alcohol, both forms are simultaneously deposited. The crystals melt at $135-136^\circ$ and are triclinic: [$a:b:c=0.73660:1:0.93952$. $\alpha=99^\circ30'$; $\beta=88^\circ7'$; $\gamma=118^\circ22'$]. A monoclinic form was also observed, but was not obtained in a stable condition. It is extremely soluble in benzene, less so in ether or ethyl acetate, and to a slight extent in alcohol or acetic acid. The values found for its molecular weight are 435—471 in freezing benzene; 530 and 541 in boiling acetic acid; 529—551 in boiling benzene, and 634 and 670 in boiling alcohol, the calculated value being 639. It resists energetically the action of oxidising agents, being unaltered by boiling with sulphuric acid and dichromate in acetic acid solution, but alkalis in alcoholic solution convert it into a brown, uncrystallisable resin. Zinc and acetic acid act on it, yielding a *reduction product* which is slightly soluble in alcohol or ether, giving solutions coloured violet by light; it dissolves in ethyl acetate, acetic acid, or benzene, crystallising from the last-named in lustrous prisms which melt at 225° and on further heating evolve chlorine.

The action of phosphorus pentachloride on 1:8-naphthalic anhydride yields an unstable naphthalyl chloride, which could not be isolated as it rapidly absorbs water from the air, being converted into naphthalic anhydride and hydrochloric acid; this instability indicates a symmetrical constitution for the chloride.

The action of potassium hypobromite on 1:8-naphthalimide in the cold yields 1:8-naphthalbromoimide, $C_{10}H_6 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} NBr$, which crystallises from benzene in lustrous, yellow laminæ decomposing at about 200° . It did not give satisfactory numbers on analysis, as it is readily converted into naphthalimide by water or alkalis.

1:8-Naphthalchloroimide, $C_{12}H_6O_2NCl$, obtained similarly to the bromo-compound, crystallises from benzene in lustrous, white plates which melt at $233-234^\circ$ and are soluble in ethyl acetate, alcohol, or chloroform. By ammonia or amines, it is reconverted into naphthalimide. When treated with hot potassium hypobromite, naphthalimide is converted in small quantity into 1:8-aminonaphthoic acid. T. H. P.

Action of Sulphuryl Chloride on the Methyl and Ethyl Esters of Gallic Acid. By GIROLAMO MAZZARA and P. GUARNIERI (*Gazzetta*, 1901, 31, ii, 184—190. Compare Abstr., this vol., i, 594).—*Methyl dichlorogallate*, $C_6Cl_2(OH)_3 \cdot CO_2Me$, obtained by the action of 2 mols. of sulphuryl chloride on methyl gallate, crystallises from water in monoclinic, prismatic plates which contain $1\frac{1}{2}H_2O$, and, when dehydrated, melt at $169-170^\circ$; it is soluble in solutions of the alkali carbonates, to which it imparts a red colour, whilst with ferric chloride solution it gives an azure coloration.

Ethyl chlorogallate, $C_6HCl(OH)_3 \cdot CO_2Et$, crystallises from water in mammillary masses of thin needles containing $1H_2O$; with alkali carbonates, it gives a yellowish, and with ferric salts an azure, coloration. The anhydrous ester melts at $106-107^\circ$.

Methyl chlorogallate, $C_6HCl(OH)_3 \cdot CO_2Me$, separates from water in

yellow prisms containing $1\text{H}_2\text{O}$, the anhydrous salt melting at $159-160^\circ$.

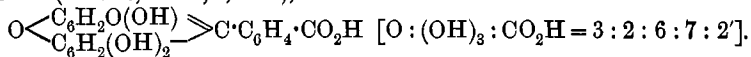
These results show that those monochloro-derivatives of the esters of gallic acid which have the halogen atom between the CO_2R group and hydroxyl crystallise with $1\text{H}_2\text{O}$, whilst the dichloro-compounds contain $1\frac{1}{2}\text{H}_2\text{O}$. Also, the methyl derivatives melt at a higher temperature than the corresponding ethyl compounds. T. H. P.

Dihydroxyfluorescein. By JOHANNES THIELE and CARL JAEGER (*Ber.*, 1901, **34**, 2617—2620).—Dihydroxyfluorescein has already been described by Liebermann (*Abstr.*, 1901, i, 595). The *ammonium* salt, $\text{C}_{20}\text{H}_{12}\text{O}_7\cdot\text{NH}_3$, is a dark green mass, which is formed by the action of gaseous ammonia on air-dried dihydroxyfluorescein and forms a reddish-brown solution in water, exhibiting a dark green fluorescence.

Dibromodihydroxyfluorescein, $\text{C}_{20}\text{H}_{10}\text{O}_7\text{Br}_2$, is a red powder which decomposes above 200° . Dihydroxyfluorescein is converted by sulphuric acid at 120° into *violetin*, $\text{CO} \begin{array}{c} \text{C}(\text{OH})\text{:CH} \\ \text{CH}=\text{C} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}(\text{OH})_2 \end{array} \text{CO}$,

which is a dark powder forming violet-coloured solutions in nitrobenzene, aniline, or acetic acid, and deep blue salts with alkalis. The *triacetate* is a dark brownish, violet powder. A. H.

The Phthalein of Hydroxyquinol. By W. FEUERSTEIN and M. DUTOIT (*Ber.*, 1901, **34**, 2637—2642).—Hydroxyquinolphthalein (dihydroxyfluorescein), which has been previously described by Liebermann (*Abstr.*, 1901, i, 595), has the constitution



This is shown by the fact that when treated with alcohol and sulphuric acid it yields an *ethyl ester*, $\text{C}_{19}\text{H}_8\text{O}_2(\text{OH})_3\cdot\text{CO}_2\text{Et}$, which crystallises in green plates melting at 326° . This ester has almost the same tinctorial properties as the original colouring matter, which shows that the two substances must be similarly constituted. The ester yields a *triacetyl* derivative, which forms hard, orange-yellow crystals, melts at $238-239^\circ$, and shows an intense fluorescence in dilute solution.

On the other hand, the action of acid chlorides on the phthalein brings about a molecular rearrangement and colourless substances are produced. Of these the tetra-acetyl derivative has already been described.

Tetrabenzoylhydroxyquinolphthalein, $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{O} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \text{C}_6\text{H}_2(\text{OBz})_2 \\ \text{C}_6\text{H}_2(\text{OBz})_2 \end{array} \text{O}$, forms large, compact crystals.

[W. FEUERSTEIN and JEAN WALLACH].—Fluorescein itself may readily be esterified directly by the action of alcohol and sulphuric acid. The ethyl ester prepared in this way is a red powder melting at 242° , whilst that obtained indirectly by Nietzki and Schröter (*Abstr.*, 1895, i, 183) is described as melting at 247° . On treatment with acetic anhydride, it yields *monoacetylfluorescein ethyl ester*, $\text{C}_{24}\text{H}_{18}\text{O}_6$, crystallising in orange-coloured needles, which have a blue surface lustre and melt at 191° . *Fluorescein methyl ester* forms red crystals with a green lustre and melts at $252-253^\circ$. A. H.

Constitution of Gallein and Cœrulein. By WILLIAM R. ORNDORFF and C. E. BREWER (*Amer. Chem. J.*, 1901, 26, 97—158. Compare Abstr., 1900, i, 447; Buchka, Abstr., 1882, 58; Herzig, Abstr., 1892, 1319).—Gallein tetra-acetate melts at 241° (Buchka gives 247 — 248° and Herzig 236 — 237°); it separates from a mixture of alcohol and chloroform in triclinic crystals, of which measurements are given. The tetrabenzoate melts at 226° (Buchka gives 231°), but it was not found possible to estimate the number of benzoyl groups by hydrolysis. Gallin tetra-acetate is an acid and the silver salt, $C_{20}H_9O_7Ac_4Ag$, was obtained as a white precipitate resembling silver chloride.

Gallein methyl ester, $C_{19}H_8O_2(OH)_3 \cdot CO_2Me$, separates from ether in dark red, granular masses with a bronze-like lustre and does not melt at 280° ; the *ethyl ester* forms crystals which are red by transmitted, and green by reflected, light.

Gallein triphenylcarbamate, $C_{20}H_9O_7(CO \cdot NHPh)_3$, is a light yellow solid which does not melt sharply on account of decomposition.

The basic lead salt, $C_{20}H_9O_7(Pb \cdot OH)_4$, is a dark blue powder and its formation can be used as a test either for lead or for gallein. The *trimethyl ether*, $C_{20}H_9O_4(OMe)_3$, forms colourless crystals, melts at 229° , and resembles phenolphthalein; the *acetate*, $C_{20}H_9O_3(OMe)_3 \cdot OAc$, crystallises from alcohol in needles and melts at 97° . *Gallein tetramethyl ether*, $C_{20}H_8O_3(OMe)_4$, exists in two modifications; the *coloured ether* forms dark red, monoclinic pyramids, melts sharply at 199° , and is readily hydrolysed by alcoholic sodium carbonate to the colourless trimethyl ether; the *colourless ether* crystallises in needles, melts at 195° , is less soluble in organic solvents than the coloured ether, and is insoluble in aqueous potassium hydroxide, even on boiling. The *coloured tetraethyl ether*, $C_{20}H_8O_3(OEt)_4$, forms dark red, monoclinic crystals and melts at 155° ; it is readily hydrolysed to the colourless triethyl ether; the *colourless tetraethyl ether* crystallises from alcohol in needles, melts at 144° , and is insoluble in boiling aqueous alkalis.

Gallin pentamethyl ether, $C_{20}H_9O_2(OMe)_5$, separates from alcohol and acetic acid in crystals which are almost white and melts at 127° .

Cœrulein triacetate was prepared by Buchka's method and the number of acetyl groups determined by hydrolysis. The acetate of cœrulein was also prepared by Buchka's method, but hydrolysis showed it to be a *penta acetate* and not a tetra-acetate; it was also found not to melt at 256° , but to decompose without melting. Cœrulein forms two *monomethyl ethers*; one separates from alcohol in dark crystals with a bronze-like lustre, decomposes without melting when heated, and dissolves to an olive-brown solution in alcohol, acetone, pyridine, aniline, or potassium hydroxide; the other is more soluble and dissolves in acetone or pyridine with a purple colour, in alcohol or aniline with a greenish-blue colour, and in aqueous potassium hydroxide with a light green colour. The *monaethyl ether* was also prepared.

T. M. L.

Caffetannic Acid. By CARL RUNDQVIST (*Chem. Centr.*, 1901, ii, 773—774; from *Pharm. Post.*, 34, 425—426).—Domingo and Guatemala coffee contain 5.928 and 6.292 per cent. of sucrose respec-

tively. The magnesium and calcium salts of caffetannic acid can be extracted from coffee by means of absolute methyl alcohol and are precipitated from the solution on the addition of ether. The free acid forms a pale yellow, flexible, transparent mass which does not attain a constant weight when allowed to remain over phosphoric oxide in a vacuum. The *hexa-acetyl* derivative, $C_{34}H_{32}O_{13}Ac_6$, forms a dusty, grey, amorphous powder which is not affected by exposure to the atmosphere, melts and decomposes at 94° , and is readily soluble in hot alcohol, acetone, or chloroform, slightly so in cold alcohol, and insoluble in water or ether. On rubbing, the powder becomes strongly electrified and when suspended in water it combines with a considerable quantity of bromine. By the action of a 5 per cent. solution of sulphuric acid on caffetannic acid, caffeic acid is formed, but since no sugar is obtained the acid cannot be regarded as a glucoside acid.

E. W. W.

Benzaldehyde-*o*-sulphonic Acid. LEVINSTEIN (LIMITED) (D.R.-P. 119163. Compare D.R.-P. 115410).—*Benzaldehyde-*o*-sulphonic acid* is prepared by oxidising calcium stilbene-*o*-disulphonate in aqueous solution with potassium permanganate; it yields on condensation with dimethylaniline a sulphonated leuco-base giving rise to a greenish-blue colouring matter identical with that described in D.R.-P. 89397. The stilbenesulphonic acid employed in this preparation is obtained from diaminostilbenedisulphonic acid (compare Bender and Schultz, Abstr., 1887, 268).

G. T. M.

Preparation of 2:5-Dimethylbenzaldehyde; the Establishment of its Constitution and Preparation of some of its Derivatives. By EVERHART P. HARDING and LILLIAN COHEN (*J. Amer. Chem. Soc.*, 1901, 23, 594—606).—An investigation as to whether, in the preparation of aldehydes by the method of Gattermann and Koch (Abstr., 1897, i, 519), the aldehyde group can enter the benzene ring without occupying the para-position to a methyl group.

2:5-Dimethylbenzaldehyde, $C_6H_3Me_2 \cdot CHO$, prepared by the above method, is a colourless liquid which boils at $219-229^\circ$ (uncorr.), has the odour of benzaldehyde, and is soluble in all the usual solvents except water; on exposure to the air, it is rapidly oxidised and becomes yellow. The *aldazine*, $C_6H_3Me_2 \cdot CH:N:N:CH \cdot C_6H_3Me_2$, forms yellow crystals, melts at $114-114.5^\circ$, and is soluble in alcohol, ether, benzene, or glacial acetic acid. The *phenylhydrazone* is obtained as a yellowish-white precipitate; when crystallised from glacial acetic acid, it melts at $84-85.5^\circ$, and is soluble in alcohol, ether, or benzene; it is unstable and rapidly darkens in colour. The *oxime* forms colourless crystals, melts at $83.5-84^\circ$, and is soluble in alcohol, ether, benzene, or acetic acid. The *benzidine* derivative forms sulphur-yellow, rhombic crystals [$a:b:c = 0.5255 + :1 : \text{approx.} 1 +$], melts at 187.5° (uncorr.), and is soluble in benzene or chloroform. The *aniline* derivative crystallises in lustrous plates, melts at 51° (uncorr.), and is readily soluble in alcohol, benzene, or light petroleum; it is decomposed by water with regeneration of aniline and the aldehyde.

2:5-Dimethylbenzoic acid, $C_6H_3Me_2 \cdot CO_2H$, obtained by shaking

the aldehyde with strong solution of sodium hydroxide, crystallises in colourless needles of the mono- or tri-clinic system [$\beta = 58^\circ 21'$], melts at $124\text{--}125^\circ$ (uncorr.), and is soluble in alcohol, benzene, chloroform, or acetone.

2:5-Dimethylcinnamic acid, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, obtained by the action of malonic acid on the aniline derivative of dimethylbenzaldehyde, crystallises in white, triclinic needles, melts at $176\cdot5^\circ$ (uncorr.), and is soluble in alcohol, ether, chloroform, benzene, light petroleum, acetone, or hot water. On reduction with sodium amalgam, it is converted into 2:5-dimethylhydrocinnamic [β :2:5-xylylpropionic] acid, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises in needles and melts at $111\cdot5^\circ$ (uncorr.).

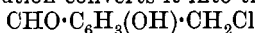
By the action of hydrogen sulphide on an alcoholic solution of dimethylbenzaldehyde, the *trithio*-derivative, $(\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CHS})_3$, is produced, which crystallises in large, colourless, monoclinic plates, melts at 110° (uncorr.), and is soluble in benzene, alcohol, or chloroform.

E. G.

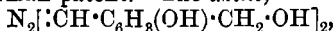
Synthesis of Aromatic Alcohols by means of Formaldehyde.

By RICHARD STOERMER and K. BEHN (*Ber.*, 1901, 34, 2455—2460).—The presence of a negative group (CHO , NO_2 , CO_2H , Cl) in the ortho-position relatively to the hydroxyl of phenols causes the latter to condense with formaldehyde in hydrochloric acid solution to form hydroxybenzyl alcohols containing the methylol group in the para-position with regard to the hydroxyl radicle.

2-Hydroxy-5-methylolbenzaldehyde, obtained from salicylaldehyde, crystallises from water in long, white needles, melts at 108° , and does not reduce solutions of silver or Fehling's solution; hydrogen chloride in absolute alcoholic solution converts it into the chloride



(German Patent 114194). The latter is probably the first product of the interaction between formaldehyde and salicylaldehyde in presence of hydrogen chloride, as on pouring off the formaldehyde solution and removing the excess of salicylaldehyde with steam, an oil remains from which water does not extract hydroxymethylol benzaldehyde; the oil is probably the *ether*, $\text{O}[\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CHO}]_2$, as it is converted by alcoholic hydrogen chloride into the chloride described in the German patent. The *azine*,



is a yellowish-white, crystalline powder melting at 219° ; the *phenylhydrazone* is similar and melts at 142° . On methylating the aldehyde-alcohol with methyl iodide, a mixture of the phenolic and alcoholic ethers is obtained, which on oxidation with alkaline potassium permanganate yields 4-methoxyisophthalic acid.

From 2-hydroxy-*m*-tolualdehyde, the compound $\text{C}_9\text{H}_{10}\text{O}_3$ is obtained, which crystallises from light petroleum in yellowish needles, melts at 83° , and yields a *chloride*, $\text{C}_9\text{H}_9\text{O}_2\text{Cl}$, crystallising from the same solvent in long, white, silky needles and melting at 82° .

3-Nitro-4-hydroxybenzyl alcohol, obtained from *o*-nitrophenol, crystallises from water in long, yellow needles, melts at 97° , and yields a *chloride*, $\text{C}_7\text{H}_6\text{O}_3\text{NCl}$, crystallising from light petroleum in long leaflets and

melting at 72° ; the *methyl* ether of the alcohol separates from water in bright yellow needles, melts at 69° , and on oxidation with potassium permanganate yields 3-nitro-4-methoxybenzoic acid.

The *benzyl alcohol* obtained from *o*-chlorophenol crystallises from benzene in small, white needles, melts at 123° , and yields a *chloride* melting at 93° . W. A. D.

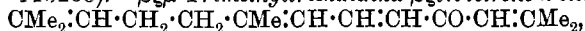
Halogen-Methyl Derivatives of the Aromatic Aldehydes. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P. 120374. Compare D.R.-P. 114194).—Derivatives of the aromatic hydroxyaldehydes containing the radicle CH_2X ($\text{X} = \text{a halogen}$) are obtained by the interaction of these aldehydes with chloro- or bromo-methyl alcohol, the reaction taking place more readily in the presence of a condensing agent such as zinc chloride, phosphorus oxychloride, or phosphoric oxide than in that of a mineral acid.

2-Hydroxy-5-bromomethylbenzaldehyde, $\text{CH}_2\text{Br}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CHO}$ (m. p. 106°), is produced by the interaction of salicylaldehyde and bromomethyl alcohol in glacial acetic acid containing zinc chloride.

Chloromethylvanillin, prepared by condensing vanillin and chloromethyl alcohol with phosphorus oxychloride, crystallises in colourless leaflets and melts at 127° . *Iodomethyl vanillin*, produced in a similar manner, separates from glacial acetic acid in yellow crystals melting at $157\text{--}158^{\circ}$. G. T. M.

Isolation of isoIrone from Bears wort Oil. HAARMANN & REIMER (D.R.-P. 120559).—*isoIrone*, $\text{C}_{18}\text{H}_{20}\text{O}$, is obtained from bears wort oil ("Kostuswüzelöl") by treating it with phenylhydrazine-*p*-sulphonic acid in the presence of sodium carbonate, distilling the acidified hydrazonesulphonic acid solution in a current of steam, and rectifying the oil under diminished pressure. The new ketone boils at $140\text{--}150^{\circ}$ under 20 mm. pressure, and has a sp. gr. 0.93 at 20° ; it yields a *p*-bromophenylhydrazone melting at $161\text{--}163^{\circ}$; the corresponding irone derivative melts at $168\text{--}170^{\circ}$. *isoIrone*, on treatment with dilute hydriodic acid, yields a hydrocarbon which, when subsequently oxidised with potassium permanganate, furnishes the acid $\text{C}_{12}\text{H}_{12}\text{O}_6$ (m. p. 214°), also produced in a similar manner from irone. G. T. M.

Ianthone; a Condensation Product of Mesityl Oxide and Lippial or Citral. DURAND, HUGUENIN & CO. and PHILIPPE BARBIER (D.R.-P. 118288).— $\beta\zeta\mu$ -Trimethyltriskaideka- $\beta\zeta\theta\lambda$ -tetrene- κ -one,



results from the condensation of citral or lippial [the lemonal from the essential oil of *Lippia citriodora* (compare Barbier, Abstr., 1899, i, 769)] with mesityl oxide in an aqueous or alcoholic solution of an alkali hydroxide or a salt having an alkaline reaction; it is a yellow oil having no characteristic odour and boils at 185° under 10 mm. pressure.

Ianthone, produced by warming the preceding substance with 60—70 per cent. sulphuric acid, is an isomeric ketone derived from tetrahydrobenzene and having two double linkings in its ketonic side chain; it is a golden-yellow oil soluble in all proportions in the alcohols, and has a characteristic odour of violets. It boils at 162°

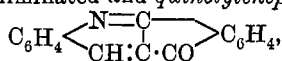
under 10 mm. pressure, and has a sp. gr. 0.9452 at 20°. Ionone is also formed in the preceding transformation, but is readily removed by means of phenylhydrazinesulphonic acid (compare D.R.-P. 73089 and 75120). G. T. M.

Preparation of Anthraphenone. By EDUARD LIPPMANN and ISIDOR POLLAK (*Ber.*, 1901, 34, 2766. Compare this vol., i, 37).—A solution of anthracene and benzoyl chloride in carbon disulphide, to which zinc dust has been added, is boiled for about three weeks, until hydrogen chloride ceases to be evolved. After removal of the carbon disulphide by distillation, the product is freed from benzoyl chloride by means of sodium hydroxide, dried on a porous plate, and recrystallised from xylene. The yield of anthraphenone is 78 per cent. of the calculated amount. K. J. P. O.

Derivatives of Diketohydrindene (Indanedione). By EMILIO NOELTING and H. BLUM (*Ber.*, 1901, 34, 2467—2471).—*p*-Dimethylaminobenzylideneindanedione, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} > C:CH \cdot C_6H_4 \cdot NMe_2$, obtained by condensing diketohydrindene with *p*-dimethylaminobenzaldehyde in alcoholic solution, crystallises from alcohol in steel-blue crystals, from benzene in scarlet masses, and melts at 99°; the *hydrochloride* is a greyish powder and is decomposed by moisture.

p-Aminobenzylideneindanedione, from *p*-aminobenzaldehyde, crystallises from alcohol in blue, lustrous leaflets and melts and decomposes at 247°. 3-Nitro-4 dimethylaminobenzylideneindanedione crystallises from alcohol in golden-yellow needles and melts at 221°.

On heating *o*-aminobenzaldehyde with diketohydrindene at 100°, 2 mols. of water are eliminated and *quinolylenephenylene ketone*,



is formed; it crystallises from alcohol, melts at 175.5°, and is slightly basic, dissolving to some extent in dilute hydrochloric acid. The *oxime*, $C_{16}H_{10}ON_2$, crystallises from alcohol in small, felted needles and melts and decomposes at 261°; the *phenylhydrazone* crystallises in beautiful, golden-yellow needles and melts at 183°; the *nitrophenylhydrazone* separates from glacial acetic acid as an orange, crystalline mass melting at 256°. *Quinolylenephenylenemethane*,

$C_6H_4 \begin{smallmatrix} \text{N}=\text{C} \\ \diagup \quad \diagdown \\ \text{CH}:\text{C}:\text{CH}_2 \end{smallmatrix} > C_6H_4$, obtained by distilling the ketone with zinc

dust, crystallises from alcohol, melts at 166—167°, and on distillation with litharge yields a red *hydrocarbon* analogous to that obtained by Graebe by the similar treatment of fluorene. W. A. D.

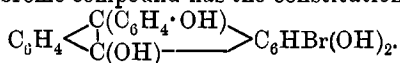
Preparation of Quinone and Quinol. THEODOR KEMPF (D.R.-P. 117251).—Benzene is readily oxidised to benzoquinone when suspended in 10 per cent. sulphuric acid in an anode cell furnished with a revolving leaden electrode coated with lead peroxide. The benzene is maintained in an emulsified condition by constant agitation and the mixture is subsequently transferred to the cathode cell where the benzoquinone is reduced to quinol (compare Gattermann and Friedrichs, *Abstr.*, 1894, i, 501). G. T. M.

$\Delta^{1,4}$ -Terpadiene-3-oxime-6-one (Nitrosothymol). By EDWARD KREMERS and I. W. BRANDEL (*Pharm. Arch.*, 1901, 4, 107—115).—Goldschmidt and Schmid (*Abstr.*, 1884, 1327) have shown that nitrosothymol is identical with thymoquinoneoxime. The author considers that by the action of nitrous acid on thymol a true nitroso-derivative is probably first formed and that this compound is unstable and readily converted into the oxime, or, possibly, a bisnitroso-derivative. The hydrolysis of nitrosothymol, with formation of thymoquinone, can be effected by heating it with syrupy phosphoric acid for several hours. E. G.

Transformation of Anthradiquinones and Anthradiquinone-imides into Hydroxyanthraquinones and Aminohydroxyanthraquinones. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P.

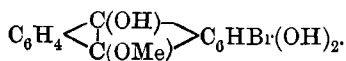
119756).—Pentacyaninequinone, $C_6H(OH)_8 \begin{smallmatrix} < \text{CO} \cdot \text{C} \cdot \text{CO} \cdot \text{CH} \\ | & | & | \\ \text{CO} \cdot \text{C} \cdot \text{CO} \cdot \text{CH} \end{smallmatrix}$, when dissolved in concentrated sulphuric acid and treated with crystallised boric acid, yields 1 : 3 : 4 : 5 : 7 : 8-hexahydroxyanthraquinone. Under these conditions, the quinoneimides of diaminoanthrarufindisulphonic acid and diaminochrysazindisulphonic acid yield respectively 4 : 8-diaminoanthrachrysone-2 : 6-disulphonic acid and 1 : 8-diamino-2 : 4 : 5 : 7-tetrahydroxyanthraquinone-3 : 6-disulphonic acid. G. T. M.

Colouring Matters of the Phenylanthracene Series. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117894. Compare D.R.-P. 109344 and following abstract).—Chloro- and bromo-deoxyalizarin, when condensed with the phenols, yield a series of colouring matters sparingly soluble in water, but dissolving readily in alkali solutions and the ordinary organic solvents. The condensation product with phenol and the bromo-compound has the constitution



Similar substances have been obtained from resorcinol, pyrogallol, salicylic acid, and β -naphthol. Bromodeoxyanthrapurpurin reacts in a similar manner with phenol. G. T. M.

Preparation of Anthracene Derivatives containing a Halogen Radicle in the Meso-Ring. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117923. Compare Romer, *Abstr.*, 1881, 823).—Deoxyalizarin and its homologues *deoxyanthrapurpurin* and *deoxyflavopurpurin*, when treated with chlorine or bromine in an indifferent solvent, yield compounds containing one of the meso-hydroxyl groups replaced by the halogen. The bromo-compound obtained from deoxyalizarin has the formula $C_6H_4 \begin{smallmatrix} < \text{CBr} \\ | \\ \text{C}(\text{OH}) \end{smallmatrix} \text{---} C_6HBr(OH)_2$; it is a very reactive substance and yields bromoalizarin when warmed with sodium hydroxide. On treatment with methyl alcohol, the compound loses bromine and yields a *methoxy*-derivative having one or other of the following constitutions, $C_6H_4 \begin{smallmatrix} < \text{CO} \\ | \\ \text{CH}(\text{OMe}) \end{smallmatrix} \text{---} C_6HBr(OH)_2$, or

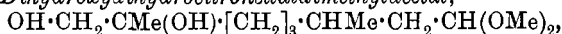


G. T. M.

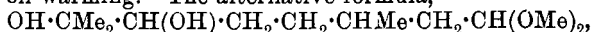
Auto-oxidation Products of Anthragallol. I. By MAX BAMBERGER and ARTHUR PRAETORIUS (*Monatsh.*, 1901, **22**, 587—589).—Anthragallol was oxidised by drawing air through a strongly alkaline solution for a considerable time. After acidifying, the presence of hydrogen peroxide was demonstrated in the dark coloured solution. On extracting with ether, a sulphur-yellow compound, $C_{12}H_{10}O_5$, was obtained, crystallising in plates, melting at 197° , and dissolving in alkalis with a blood-red colour. The silver salt, $C_{12}H_8O_5Ag_2$, prepared by boiling an aqueous solution of the compound with silver carbonate, crystallises in violet-red needles. A methyl derivative, $C_{12}H_9O_5Me$, prepared by the action of methyl sulphate on a solution of the compound in dilute potassium hydroxide, crystallises in yellow needles melting at 135° and soluble in alkalis. K. J. P. O.

Anthrapurpurin Diacetate. KNOLL & Co. (D.R.-P. 117730).—*Anthrapurpurin diacetate*, prepared by acetylating anthrapurpurin with an equal weight of acetic anhydride or chloride, or with glacial acetic acid and phosphorus oxychloride, is a greenish-yellow powder melting at 175 — 178° ; it is hydrolysed by alkali hydroxides or carbonates and also by the juices of the intestine. G. T. M.

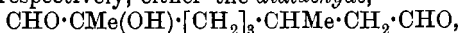
Constitution of Citronellaldehyde. By CARL D. HARRIES and OTTO SCHAUWECKER (*Ber.*, 1901, **34**, 2981—2991. Compare this vol., i, 448).—*Dihydroxydihydrocitronellaldimethylacetal*,



produced by oxidising citronellaldimethylacetal with potassium permanganate in dilute acetone solution (Sachs, this vol., i, 272), is an oil boiling at 151 — 153° under 9 mm. pressure and having a sp. gr. 1.0053 at 11° ; it does not reduce Fehling's solution even on warming. The *dihydroxyaldehyde*, obtained by boiling the preceding compound with dilute hydrochloric acid, is an unstable oil boiling at 158 — 162° under 22 mm. pressure; it has a pungent odour and reduces Fehling's solution on warming. The alternative formula,

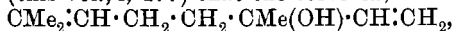


for the preceding glycol-acetal is excluded by the fact that on oxidation with 1 or 3 atomic proportions of oxygen derived from chromic acid, it yields respectively, either the *dialdehyde*,

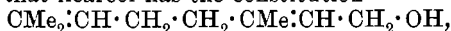


a viscid, colourless oil boiling at 138 — 140° under 10 mm. pressure, or the *ketoaldehyde* (3-methyloctanone-7-al), a yellow liquid boiling at 115 — 118° under 16—17 mm. pressure. These compounds have aldehydic odours and properties; they reduce Fehling's solution and develop a coloration with rosaniline sulphite; the dialdehyde also polymerises under the influence of mineral acids or alkalis. Both substances give rise to oily phenyl- and *p*-bromophenyl-hydrazones, but the ketoaldehyde yields a crystalline disemicarbazone forming white leaflets and melting at 244 — 245° , whilst that from the dialdehyde is oily. The *acetal*, $COMe \cdot [CH_2]_3 \cdot CHMe \cdot CH_2 \cdot CH(OMe)_2$, of the ketoaldehyde, an oil boiling at 130 — 135° under 14 mm. pressure, is formed in small amount during the preparation of the aldehyde; it yields an oily phenylhydrazone, but does not reduce Fehling's solution. G. T. M.

Constitution of Licareol (Linalool). By PHILIPPE BARBIER (*Bull. Soc. Chim.*, 1901, [iii], 25, 828—832).—It has been shown in a previous paper (this vol., i, 477) that the formula,



formerly assigned to licareol, belongs in reality to myrcenol, and it is now suggested that licareol has the constitution

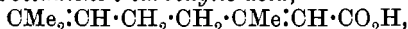


and is stereoisomeric with lemonol. The oxidation products of licareol are identical with those of lemonol, and it is shown that all the reactions of licareol are simply explained by the formula proposed. The experiments of the author and others point to the conclusion that pure licareol would be found to be optically inactive, a result which is in accordance with the new, but not with the old, formula. N. L.

Chloromethyl Menthyl Oxide. EDGAR WEDEKIND (D.R.-P. 119008).—*Chloromethyl menthyl oxide*, $\text{C}_{10}\text{H}_{19}\text{O}\cdot\text{CH}_2\text{Cl}$, prepared by saturating a mixture of menthol and formalin solution with hydrogen chloride at the temperature of the water-bath, is a colourless, highly refractive oil boiling at $160\text{--}163^\circ$ under 13—16 mm. pressure; it has $[\alpha]_D -172.57^\circ$ at 27° and a sp. gr. 0.9821 at 4° . This ether is very easily resolved into menthol, formaldehyde, and hydrogen chloride by the action of water, and undergoes partial decomposition when distilled under reduced pressure, yielding methylenedimenthyl ether, $\text{C}_{21}\text{H}_{40}\text{O}_2$. G. T. M.

$\beta\zeta$ -Dimethyl- $\beta\epsilon$ -octadiene- θ -al, an Isomeride of Citral. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 118351).— $\zeta\zeta$ -Dichloro- β -methylheptene, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMeCl}_2$, obtained by the action of phosphorus pentachloride on methylheptenone, $\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ac}$, loses hydrogen chloride when heated on the water-bath, yielding ζ -chloro- β -methylhepta- $\beta\epsilon$ -diene, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CMeCl}$. The monochloro-derivative, when condensed with the sodium derivative of ethyl malonate in boiling alcohol, yields diethyl $\beta\zeta$ -dimethyl- $\beta\epsilon$ -octadiene- $\eta\theta$ -dicarboxylate, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}(\text{CO}_2\text{Et})_2$.

$\beta\zeta$ -Dimethyl- $\beta\epsilon$ -octadiene- θ -carboxylic acid,



is produced on distilling the dicarboxylic acid under reduced pressure; it boils at 160° under 12 mm. pressure and is isomeric with geranic acid.

$\beta\zeta$ -Dimethyl- $\beta\epsilon$ -octadiene- θ -al, prepared by heating an intimate mixture of barium formate and the barium salt of the preceding acid, boils at $225\text{--}230^\circ$; its *semicarbazone* melts at 145° and its condensation product with cyanoacetic acid at 130° ; the *oxime* and *phenylhydrazone* are oils. G. T. M.

$\beta\zeta$ -Dimethyl- $\beta\epsilon$ -octadiene- θ -al. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 119043. Compare preceding abstract).—The ethyl malonate employed in preparing $\beta\zeta$ -dimethyl- $\beta\epsilon$ -octadiene- $\eta\theta$ -dicarboxylic acid may be replaced by ethyl cyanoacetate, the intermediate product, η -cyano- $\beta\zeta$ -dimethyl- $\beta\epsilon$ -octadiene- θ -carboxylate, being hydrolysed to the potassium dicarboxylate by 30 per cent. potassium hydroxide.

Ethyl acetoacetate, when employed in this condensation, gives rise

to *ethyl βξ-dimethyl-βε-nonodiene-θ-one-η-carboxylate*, this product yielding the potassium dicarboxylate on treatment with 33 per cent. potassium hydroxide solution. G. T. M.

Reduction in the Terpene Series. Myrcene and other Olefinic Compounds. By FRIEDRICH W. SEMMLER (*Ber.*, 1901, **34**, 3122—3130).—It is shown that in the terpene series the only compounds reduced when treated with sodium and ethyl alcohol are those which contain two double linkings attached to two adjacent carbon atoms.

When reduced with sodium and alcohol, myrcene yields a *dihydromyrcene*, $C_{10}H_{18}$, which boils at $171.5-173.5^\circ$, has a sp. gr. 0.7802 and n_D 1.4501, and when treated with a mixture of acetic and sulphuric acids yields *cyclodihydromyrcene*, $OMe \begin{array}{c} \text{CH} \text{---} \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CHMe} \cdot \text{CMe}_2 \end{array} \text{CH}_2$; this boils at $169-172^\circ$, has a sp. gr. 0.828 and n_D 1.462, forms a *dibromide* of sp. gr. 1.524, and when oxidised yields a *ketonic acid*, $C_{10}H_{18}O_3$. Dihydromyrcene, when oxidised with potassium permanganate, yields *lævulic acid* and a *ketoglycol*, $C_8H_{16}O_3$, which, when oxidised with chromic acid, forms the *diketone*, $C_7H_{12}O_2$. R. H. P.

Oil of Jasmine Blossoms. By ALBERT HESSE (*Ber.*, 1901, **34**, 2916—2932. Compare Abstr., 1900, i, 454; this vol., i, 220 and 601).—The small yield of oil obtained when jasmine flowers are subjected to steam distillation is due to the fact that the greater part of the volatile oil remains dissolved in the distillate, and may be recovered by extraction with ether, the yield being about 0.0194 per cent. The oil has a sp. gr. 0.968 at 15° , a rotation of $+4^\circ 15'$ in a 100 mm. tube, and a saponification number 148. It contains benzyl acetate, free benzyl alcohol, methyl anthranilate, and little or no indole, and resembles the oil obtained by extraction, except for the presence of methyl anthranilate.

The main differences between the oils obtained by the methods of extraction, steam distillation, and 'enfleurage' are that the extracted oil is free from both indole and methyl anthranilate, the distilled oil contains practically no indole, but 1.5 per cent. of anthranilate, and the oil from 'enfleurage' 2.5 per cent. of indole, and only 0.24—0.3 per cent. of methyl anthranilate.

The oil has been extracted from the blossoms which had already undergone 'enfleurage,' and it is found that the amount present is practically identical with that in the fresh blossoms; the process of 'enfleurage' thus produces some nine times the amount of oil originally present. The oil obtained from the blossoms after 'enfleurage' contains 1.5 per cent. of methyl anthranilate, but no indole. It would thus appear that methyl anthranilate does not exist as such in the fresh blossoms, but is produced during 'enfleurage' and steam distillation.

The name *ethereal jasmine oil* is suggested for the oil obtained by extraction with volatile solvents or by steam distillation, the name in the latter case to include the greater part of the oil which remains dissolved in the water, and the expression *ethereal oil of jasmine blossoms* is to be retained for the 'enfleurage' oil. J. J. S.

Essential Oil of Orange Blossoms. I. By ALBERT HESSE and OTTO ZEITSCHEL (*J. pr. Chem.*, 1901, [ii], **64**, 245—260. Compare this vol., i, 220, and preceding abstract).—A larger yield of oil is obtained by distillation than by maceration, extraction, or enfleurage. The esters present in the oil, namely, linalyl acetate and methyl anthranilate, remain nearly unchanged in the distillation.

Pure linalyl acetate, prepared from sodium linaloolate and acetic anhydride and fractionated under reduced pressure, boils at 96·5—97° under 10 mm., 115—116° under 25 mm., and at 220° (with decomposition) under atmospheric pressure, has a sp. gr. 0·913 at 15°, [α]_D -6°35', and a saponification number 278·9.

A detailed examination of the oil is being made. K. J. P. O.

A New Aldehyde from Oil of Lemons. By HUGO VON SODEN and WILHELM ROJAHN (*Ber.*, 1901, **34**, 2809—2811).—When lemon oil, freed from citral by Tiemann's method (*Abstr.*, 1899, i, 247), and from non-volatile constituents by distillation, is shaken with acid sodium hydrogen sulphite solution, a mixture of nonaldehyde with some octaldehyde is obtained in the form of the bisulphite compound. The authors are of opinion that the aldehyde isolated by Burgess (*Proc.*, 1901, 17, 171) is nonaldehyde, and point out that the fluorescent substance (m. p. 145°) obtained by him was first described by Crismer (*Abstr.*, 1892, 349), and subsequently by Theulier (this vol., i, 218).

R. H. P.

Oil of Neroli. By HEINRICH WALBAUM (*Ber.*, 1901, **34**, 2603).—An explanation, in reply to E. and H. Erdmann (this vol., i, 601).

C. F. B.

Occurrence of Phenylethyl Alcohol in Oil of Roses. By HUGO VON SODEN and WILHELM ROJAHN (*Ber.*, 1901, **34**, 2803—2809. Compare *Abstr.*, 1900, i, 489, and this vol., i, 39).—It is shown that oil of roses contains up to 60 per cent. of phenylethyl alcohol. The method of separating this alcohol from crude oil of roses is described.

The aqueous distillate obtained in the distillation of ylang-ylang oil contains benzyl alcohol, which is a normal, although unimportant, constituent of the oil.

R. H. P.

Essence of Thyme. By PAUL JEANCARD and C. SATIE (*Bull. Soc. Chim.*, 1901, [iii], **25**, 893—895).—It is generally considered that essence of thyme should contain 25—30 per cent. of phenols, but a number of pure specimens were found to contain from 5—60 per cent. This variation depends on the manner in which the distillation is conducted, as is shown by an examination of essence of red Algerian thyme and essence of ajowan. The greater portion of the phenols passes over in the later stages of the distillation. The sp. gr. of the different fractions increases by 0·0013—0·0015 for each 1 per cent. of phenols. The surface tension, viscosity, and solubility in alcohol also increase with the proportion of phenols.

N. L.

Behaviour of Caoutchouc towards Nitrous Acid. By CARL D. HARRIES (*Ber.*, 1901, **34**, 2991—2992).—Caoutchouc, when dis-

solved or suspended in light petroleum and subjected to the action of a rapid current of nitrous fumes evolved from arsenious oxide and nitric acid, yields a colloidal mass which gradually changes into a golden-yellow, flaky compound. This substance readily dissolves in ethyl acetate and is reprecipitated in a granular form on adding ether; it sinters at 95—100° and decomposes at 135°. Analyses and molecular weight determinations by the boiling point method indicate the empirical formula $C_{40}H_{62}O_{24}N_{10}$; the substance is acidic, being dissolved by dilute alkaline solutions and reprecipitated by acids.

G. T. M.

Rhododendrol, Rhododendrin, and Andromedotoxin. By KONSTANTIN ARCHANGELSKI (*Chem. Centr.*, 1901, ii, 594—595; from *Arch. exp. Path. Pharm.*, 46, 313—320).—The leaves of *Rhododendron chrysanthum* contain the glucoside ericolin (Thal, *Pharm. Zeit. Russ.*, 1883, 209), andromedotoxin (Eykmán, *Abstr.*, 1883, 349; Plugge, *Abstr.*, 1889, 644), and rhododendrin, together with rhododendrol, a decomposition product of rhododendrin resembling camphor. *Rhododendrol*, $C_{10}H_{12}O_2$, crystallises from water in long, colourless needles or small plates, melts at 79.5—80°, sublimes without decomposition, and is easily soluble in hot but only slightly so in cold water. When heated with nitric acid, it gives a red coloration, which becomes yellow on the addition of alkali. Its physiological effect on frogs is similar to that of camphor but on warm blooded animals it has not a poisonous effect, being excreted in the urine probably in combination with glycuronic acid. *Rhododendrin*, $C_{16}H_{22}O_7$, crystallises from water, melts at 187—187.5°, has a bitter taste, and is easily soluble in hot water or alcohol, slightly so in cold water, and only very sparingly so in chloroform or ether. It is decomposed by boiling with dilute acids forming rhododendrol and a sugar which yields an osazone melting at 194—195°. Rhododendrin has no pharmacological action. The physiological action of andromedotoxin on frogs and mammals resembles that of digitalin in its effect on the heart.

E. W. W.

Yellow Colouring Matters accompanying Chlorophyll and their Spectroscopic Relations. By C. A. SCHUNCK (*Proc. Roy. Soc.*, 1901, 68, 474—480. Compare *Abstr.*, 1900, ii, 36).—The alcoholic extract of healthy green leaves, after removal of the chlorophyll, was submitted to a process of fractional extraction with carbon disulphide, and the several extracts thus obtained were submitted to spectroscopic examination. From the results obtained the author concludes that the four-banded spectrum of the crude solutions of the xanthophylls is due to a mixture of colouring matters, the chief of which is chrysophyll, which is identical with Sorby's orange xanthophyll (*Proc. Roy. Soc.*, 1873, 21, 457), and is not due, as he formerly supposed, to a single substance which he termed xanthophyll (*Abstr.*, 1900, ii, 36). If a small quantity of hydrochloric acid is added to a solution of chrysophyll, the effect on the spectrum is to cause the bands to fade and the solution to become gradually colourless.

H. R. LE S.

Phthalic Acid Colouring Matters of the Naphthalene Series. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 118077).—*m*-Diethylaminohydroxybenzoylbenzoic acid and its di- and tetra-

chloro-derivatives yield a series of colouring matters when condensed with the sulphonic acids of the naphthols and dihydroxynaphthalenes in the presence of 50—80 per cent. sulphuric acid at 140°. These condensation products are amorphous, and their properties are exhibited in tabular form. G. T. M.

Pyromucic Anhydride. By ERICH BAUM (*Ber.*, 1901, 34, 2505—2506).—Pyromucic chloride is converted by pyridine in aqueous ethereal solution into the *anhydride*, $C_{10}H_8O_5$, according to Wedekind's reaction (this vol., i, 499); it crystallises from alcohol in slender, white needles, melts at 73°, boils with slight decomposition at 325°, and with phenylhydrazine yields the phenylhydrazide of the acid.

W. A. D.

7-Hydroxychromone. By STANISLAUS VON KOSTANECKI, L. PAUL, and JOSEF TAMBOR (*Ber.*, 1901, 34, 2475—2479. Compare this vol., i, 558).—*Ethyl 2:4-diethoxybenzoyl pyruvate*, obtained by condensing resacetophenone diethyl ether with ethyl oxalate by means of sodium, crystallises from alcohol in yellowish needles and melts at 152°. *Ethyl 2:5-diethoxybenzoyl pyruvate*, obtained similarly from quinacetophenone diethyl ether, forms yellow prisms and melts at 90°; *ethyl 2:4:6-trimethoxybenzoyl pyruvate*, obtained from phloracetophenone trimethyl ether, crystallises in yellowish needles and melts at 80°.

Ethyl 2-hydroxy-4-ethoxybenzoyl pyruvate, obtained by the condensation of resacetophenone monoethyl ether and ethyl oxalate, crystallises from alcohol in well-formed, white needles, melts at 99—100°, and on hydrolysis with alcoholic hydrochloric acid yields *7-ethoxychromone-2-carboxylic acid*, $OEt \cdot C_6H_4 \begin{smallmatrix} O-C \cdot CO_2H \\ \diagup \quad | \\ CO \cdot CH \end{smallmatrix}$; this crystallises from alcohol in rosettes of prismatic needles, melts at 234°, and is thus converted into *7-ethoxychromone*, $OEt \cdot C_6H_4 \begin{smallmatrix} O-CH \\ \diagup \quad | \\ CO \cdot CH \end{smallmatrix}$, which separates from dilute alcohol in long needles melting at 120—121°. *7-Hydroxychromone*, obtained by elimination of the ethyl group by hydriodic acid, crystallises from water in white sheaves of needles and melts at 218°. W. A. D.

Studies in the Chromone Series. By STANISLAUS VON KOSTANECKI and LORENZO LLOYD (*Ber.*, 1901, 34, 2942—2950. Compare this vol., i, 222).—*Propionylresorcinol monoethyl ether*, $OH \cdot C_6H_3(COEt) \cdot OEt$, [$OH : OEt : COEt = 1 : 3 : 6$], obtained when propionylresorcinol (*Abstr.*, 1891, 447) is alkylated by Kostanecki and Tambor's method (*Abstr.*, 1896, i, 44), crystallises from alcohol in colourless needles melting at 54°; the *diethyl ether*, $COEt \cdot C_6H_3(OEt)_2$, forms colourless plates melting at 72°.

7-Ethoxy-2:3-dimethylchromone, $OEt \cdot C_6H_3 \begin{smallmatrix} O-CMe \\ \diagup \quad | \\ CO \cdot CMe \end{smallmatrix}$, is formed when the monoethyl ether is gently boiled for 3 hours with acetic anhydride and dry sodium acetate; it crystallises from alcohol in thick prisms melting at 124°, and gives a blue fluorescence with concentrated sulphuric acid. On hydrolysis with concentrated hydriodic acid, it yields

7-hydroxy-2:3-dimethylchromone, which crystallises in rhombic prisms melting at 262° . Its *acetyl* derivative forms long needles melting at 116° , and its ethyl ether, *7-methoxy-2:3-dimethylchromone*, is identical with Nagai's dehydromethylacetylpaenol (Abstr., 1892, 845). The same compound is readily obtained when propionylresorcinol is methylated according to Tabara's method, and the monomethyl ether thus obtained is boiled with acetic anhydride and dry sodium acetate.

2:4-Diethoxybenzoylmethylacetone, $C_6H_3(OEt)_2 \cdot CO \cdot CHMeAc$, obtained by the action of sodium and ethyl acetate on propionylresorcinyl-diethyl ether, or by the methylation of *2:4-diethoxybenzoylacetone* (Bloch and Kostanecki, Abstr., 1900, i, 308), forms colourless plates melting at 72.5° , and when heated with hydriodic acid yields *7-ethoxy-2:3-dimethylchromone*.

Nagai's hydroxyacetylpaenol is undoubtedly *4-methoxybenzoylacetone*.
J. J. S.

Colouring Matters of the Æsculetin Series. By CARL LIEBERMANN and FRITZ WIEDERMANN (*Ber.*, 1901, 34, 2608—2617).—Æsculetin unites with sodium hydrogen sulphite to form *sodium dihydroæsculetinsulphonate*, $C_6H_2(OH)_2 \begin{matrix} O-CO \\ \diagdown \quad \diagup \\ CH_2-CH-SO_3Na \end{matrix}$, which is not decomposed by dilute acids and is converted by acetic anhydride into diacetylæsculetin. *Dihydroæsculetinsulphonic acid* is a hygroscopic, crystalline mass, which decomposes, when heated, into water, sulphur dioxide, and æsculetin. The sodium salt is formed from æsculetin by the combination of the sodium hydrogen sulphite with the two doubly-linked carbon atoms. Sodium dihydroæsculetinsulphonate is converted by gaseous ammonia into a deep violet-coloured compound, which was described by Rochleder (*Weiner akad. Ber.*, 1864, 48, ii, 236; 1867, 55, ii, 829) as æscorcein, $C_9H_7O_5N$, but is in reality *sodium æscorceinsulphonate*, $C_{18}H_{12}O_{16}N_2S_2Na_6$. The aqueous solution is coloured blue, and shows a blood-red fluorescence. A similar compound, which, however, contains less sodium, $C_{18}H_{13}O_{16}N_2S_2Na_5$, may be obtained by the action of ammonia on the sulphonic acid, followed by treatment of the product with sodium ethoxide in alcoholic solution.

It is converted by bromine into a *dibromo*-derivative, the sodium salt of which has the formula $C_{18}H_{11}O_{16}Br_2N_2S_2Na_5$.

Hydroæsculetin, $C_{18}H_{14}O_8$, obtained by the reduction of æsculetin with sodium amalgam, appears to be identical with the æscorcin of Rochleder, and is converted by gaseous ammonia into *dehydroæscorcein*, $C_{18}H_{13}O_7N_3$, which is a deep violet-coloured mass, and forms a blue solution in alkalis. Æsculetin itself and its direct derivatives do not yield coloured substances with ammonia, whilst the reduction products of these substances behave in a similar manner to hydroæsculetin.
A. H.

Cactus Alkaloids. IV. By ARTHUR HEFFTER (*Ber.*, 1901, 34, 3004—3015. Compare Abstr., 1895, i, 120; 1896, i, 267; 1898, i, 499).—Anhalamine, isolated by Kauder (Abstr., 1899, i, 650) from the mezcal buttons of *Anhalonium Lewinii*, yields a *hydrochloride*,

$C_{11}H_5O_3N \cdot HCl$, crystallising slowly from water in lustrous leaflets with $2H_2O$, and from alcohol in needles with $1H_2O$; the *sulphate*, $(C_{11}H_{15}O_3N)_2 \cdot H_2SO_4$, forms colourless prisms very soluble in water, but dissolving less readily in alcohol. The *platinichloride*, $(C_{11}H_{15}O_3N)_2 \cdot H_2PtCl_6$, and the *aurichloride* crystallise respectively in yellow needles and nodules, the latter salt readily decomposing and becoming dark red. Anhalamine is optically inactive, and contains two methoxyl groups. The third oxygen atom is probably present as hydroxyl, for the alkaloid dissolves in potassium hydroxide solution, and yields a *dibenzoyl* derivative, $C_{11}H_{13}O_3NBz_2$, crystallising from alcohol or chloroform in prisms melting at $128-129^\circ$, and a *monobenzoyl* derivative, $C_{11}H_{14}O_3NBz$, melting at 167.5° . The latter product dissolves in sodium hydroxide solution and develops a blue coloration with ferric chloride. The dibenzoyl compound is insoluble in aqueous alkali hydroxides, and does not react with ferric chloride. These results indicate that anhalamine is a secondary base, having the formula $OH \cdot C_9H_7(OMe)_2 \cdot NH$.

Mezcaline, on oxidation with potassium permanganate first at the ordinary temperature and then at 100° , yields 2:3:4'-trimethoxybenzoic acid and a small amount of a neutral substance containing nitrogen and melting at 177° . The alkaloid is a secondary base, for its methiodide when shaken with chloroform yields *methylmezcaline*, a crystalline base, which in turn gives rise to a *methiodide*, $C_{12}H_{19}O_3N \cdot MeI$, crystallising in pale yellow plates and melting at 220° ; the corresponding *platinichloride* forms needles. *Benzoylmezcaline*, $C_{11}H_{16}O_3NBz$, readily produced by the Schotten-Baumann method, crystallises in lustrous needles and melts at 120.5° . These results indicate that mezcaline has the constitution

$C_6H_2(OMe)_3 \cdot CH_2 \cdot NHMe$ [$CH_2 \cdot NHMe : (OMe)_3 = 1 : 3 : 4 : 5$], and hence it may be termed 3:4:5-trimethoxybenzylmethylamine.

Mezcaline or its hydrobromide readily yields *dibromomezcaline* when suspended in water and treated with bromine. The *hydrobromide* of the dibromo-base crystallises in felted needles and melts at 95° ; the *hydrochloride* separates in lustrous prisms and the *sulphate*, $(C_{11}H_{15}O_3NBr_2)_2 \cdot H_2SO_4 \cdot 2\frac{1}{2}H_2O$, in white needles. The *platinichloride*, crystallises in hexagonal plates melting at 230° and the *aurichloride* in orange coloured needles decomposing at 191° . The dibromo-base is only slowly oxidised by potassium permanganate even in boiling solutions, and yields dibromo-2:3:4-trimethoxybenzoic acid.

Anhalonidine, when treated with excess of benzoic chloride by the Schotten-Baumann process, yields *benzoylanhalonidine benzoate*, $C_{12}H_{13}O_3NBz_2$, a compound insoluble in sodium hydroxide solution, crystallising in prisms, and melting at $125-126^\circ$. *Benzoylanhalonidine* is precipitated by ammonium chloride from the alkaline mother liquor obtained in the benzylation; it crystallises in lustrous plates and melts at 189° ; its alcoholic solution develops a blue coloration with ferric chloride. These results point to the presence of one hydroxyl group, and one imino-radicle in the molecule of anhalonidine. This assumption is confirmed by the behaviour of the base towards methyl iodide; *methylanhalonidine hydriodide* results from the interaction of these substances in boiling methyl alcohol; it crystallises in

yellow prisms and melts at 125—130°. Methylanhalonidine is an uncrystallisable base yielding crystalline salts; the *hydrochloride* forms needles and the *methiodide*, $C_{13}H_{17}O_3N, MeI, H_2O$, colourless plates or prisms sparingly soluble in cold water and melting at 199°. The iodide rendered alkaline with ammonia behaves like a solution of a quaternary base producing paralysis of the peripheral motor-nerve endings. The corresponding *platinichloride*, $(C_{14}H_{20}O_3N)_2PtCl_6$, crystallises from water in golden-yellow leaflets.

Although the constitution of anhalonidine is not yet completely determined, the foregoing results show that it may be provisionally represented by the formula $OH \cdot C_{10}H_7(OMe)_2 \cdot NH$. G. T. M.

Occurrence of Alkaloids and Saponins in Cactaceæ. By GEORG HEYL (*Arch. Pharm.*, 1901, 239, 451—473).—*Pilocereus Sargentianus* contains 92 per cent. of water; from the dry drug, 7.0 per cent. of crude (5.8 of pure) alkaloid was obtained. This alkaloid, *pilocereine*, $C_{30}H_{44}O_4N_2$, is amorphous and melts at 82—86°; its *platinichloride*, with H_2PtCl_6 , and *aurichloride*, with $2HAuCl_4$, were analysed. When heated with hydriodic acid by Zeisel's method, silver iodide is precipitated equivalent to 13.48 per cent. of methoxyl; some ethoxyl is undoubtedly present, however, for when the alkaloid is distilled with aqueous potassium hydroxide, the distillate gives the iodoform reaction. This alkaloid is a poison, causing cessation of the heart's action; the lethal dose for rabbits is 0.1 gram per kilogram of body-weight.

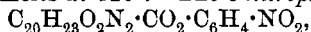
Cereus pecten aboriginum contains an alkaloid, *pectenine*, which resembles the alkaloids of *Anhalonium* in its colour reactions and physiological action. It is soluble in water and was only obtained as a syrup; a crystalline hydrochloride was prepared, however, in amount equal to 0.65 per cent. of the drug. The *platinichloride* contains Pt 23.02 per cent. The alkaloid is a poison, acting on the central nervous system and producing death by tetanic convulsions; 0.075 gram per kilogram killed a rabbit in 5 minutes.

Cereus gummosus contains no alkaloid, but a saponin, *cereic acid*, to the extent of 24 per cent. of the dry drug; the plant contains 74 per cent. of water. Cereic acid is an amorphous substance, soluble in water with an acid reaction; the solution lathers readily, especially when a little alkali is added. It contains C 58.42 and H 8.35 per cent., but no nitrogen. When it is boiled with a dilute mineral acid, insoluble *cereus sapogenin* is precipitated and the solution acquires the power of reducing Fehling's solution. When added to a mixture of a little blood with dilute salt solution, cereic acid causes the blood corpuscles to dissolve, and is about as effective in this respect as *Quillaya-sapotoxin*. Unlike this substance, however, it is only slightly poisonous; to kill a rabbit, a dose of more than 0.1 gram per kilogram is necessary.

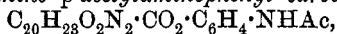
C. F. B.

Preparation of Mixed Carbonates of the Cinchona Alkaloids and the Mono- and Di-hydric Phenols. VEREINIGTE CHININ-FABRIKEN ZIMMER & Co. (D.R.-P. 117095. Compare D.R.-P. 91370).—*Quinine phenyl carbonate*, $C_{20}H_{23}O_2N_2 \cdot CO_2Ph$, prepared by heating

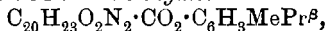
quinine and phenyl carbonate at 120—130°, crystallises from ether or light petroleum and melts at 129°. The *o*-nitrophenyl ester,



melts at 187°. *Quinine p-acetylaminophenyl carbonate*,



produced by the action of *p*-acetylaminophenol on quinine dissolved in hot xylene, melts at 184°. The *thymol* derivative,



crystallises in leaflets melting at 172°; the *catechol* compound melts at 184—185°. *Cinchonidine phenyl carbonate*, $\text{C}_{19}\text{H}_{21}\text{ON}_2\cdot\text{CO}_2\text{Ph}$, melts at 89°. These compounds are obtained as colourless, tasteless, crystalline products, sparingly soluble in water or ether, but dissolving more readily in the other organic solvents; they have a basic character and combine the therapeutic action of the alkaloids and the phenols.

G. T. M.

Preparation of Quinine and Cinchonidine Alkyl Carbonates.

VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 118352. Compare preceding abstract and D.R.-P. 91370).—The alkyl carbonates of quinine and cinchonidine are readily obtained by treating the anhydrous salts of these alkaloids with the alkyl chlorocarbonate in an indifferent solvent such as benzene.

Quinine benzyl carbonate, produced by the action of benzyl chlorocarbonate on quinine salts, crystallises in white needles and melts at 110°; it is readily soluble in the ordinary organic solvents.

G. T. M.

Quinine and Cinchonidine Chlorocarbonates.

VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 118122. Compare D.R.-P. 90868 and 93698 and preceding abstract).—*Quinine chlorocarbonate* is readily obtained by the action of carbonyl chloride (1 mol.) on dry quinine hydrochloride or sulphate suspended in cold chloroform; the corresponding *cinchonidine* salt is prepared in a similar manner.

G. T. M.

Oxidation of Conhydrine. By RICHARD WILLSTÄTTER (*Ber.*, 1901, 43, 3166—3171).—On oxidation with chromic acid, conhydrine yields *l*-pipecolic acid (*l*-piperidine-2-carboxylic acid) which melts and decomposes indefinitely at about 264—265° and has $[\alpha]_D - 24.7^\circ$ at 24°; Mende's synthetical *l*-acid (*Abstr.*, 1897, i, 203) melts at 270° and has $[\alpha]_D - 35.7^\circ$ at 20°, so that during the oxidation of conhydrine partial racemisation of the acid probably occurs. The *hydrochloride* of the *l*-acid crystallises from alcohol in sheaves of needles and melts and decomposes at 256—258°; the *copper* salt, with $3\text{H}_2\text{O}$, crystallises in deep blue rhombs and is transformed by alcohol into a salt with 1 mol. $\text{C}_2\text{H}_6\text{O}$, which forms slender, bright blue, silky needles.

The above facts show that the hydroxyl group of conhydrine is in the side-chain; the alkaloid is probably the active form of 2- β -hydroxypropylpiperidine, $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, since both conhydrine and the inactive base boil at the same temperature (224—226°).

W. A. D.

Reduction of Granatonineoxime and of Methylgranatonine.

By ANTONIO PICCININI and G. CORTESE (*Gazzetta*, 1901, 31, i, 561—570).—*Granatonineoxime*, $C_8H_{14}ON_2$, prepared by a method similar to that given by Piccinini and Quartaroli (*Abstr.*, 1899, i, 965) for the oxime of methylgranatonine, separates from a mixture of alcohol and ether in shining, colourless needles, softening at 180° and melting at 199° . Its *benzoyl* derivative, $C_{22}H_{22}O_3N_2$, crystallises from alcohol in lustrous prisms melting at 165° . The *picrate*, $C_{14}H_{17}O_8N_5$, is precipitated in needles which dissolve readily in alcohol or ether, decompose slightly at 215° , and melt at 230° .

When reduced with sodium and amyl alcohol, granatonineoxime yields ψ -granatylamine, $C_8H_{16}N_2$, which crystallises from dry, light petroleum in small, colourless, hygroscopic prisms melting at 125° ; it rapidly absorbs carbon dioxide from the air. With phenylthiocarbimide, it yields ψ -granatylphenylthiocarbimide, $C_{22}H_{20}N_4S_2$, which separates from methyl alcohol as a colourless, amorphous powder melting at 216° . The *picrate* of the amine, $C_{20}H_{22}O_{14}N_8$, crystallises from alcohol in small, yellow prisms which decompose without melting at between 230° and 247° . The *platinichloride*, forming pale orange-yellow prisms melting at 256° and the *aurichloride*, yellow prisms melting and slightly decomposing at 208° , were also prepared. When the oxime is reduced by means of sodium amalgam and acetic acid, ψ -granatylamine is formed, together with an isomeric amine; the latter could not be separated, but its *aurichloride*, $C_8H_{16}N_2 \cdot H_2Au_2Cl_8$, is deposited in the form of long, golden-yellow, thread-like crystals melting at 238 — 239° .

When reduced with either zinc and acetic acid, tin and hydrochloric acid, or sodium and amyl alcohol, methylgranatonine is completely converted into methylgranatoline. The latter is also formed, but not as sole product, when the reduction is effected with sodium amalgam and water, *methylgranatonine pinacone*, $C_{18}H_{32}O_2N_2$, being also formed in this case. This compound crystallises from alcohol in colourless, acicular prisms melting at 248° ; it is slightly soluble in water, benzene, or ether, and forms salts with acids. Its *aurichloride*, $C_{18}H_{32}O_2N_2 \cdot H_2Au_2Cl_8$, separates from water in yellow prisms melting at 229° , whilst the *platinichloride* is deposited from dilute hydrochloric acid in prisms which decompose at about 260° , leaving a residue melting at 285° . The *picrate*, $C_{30}H_{38}O_{16}N_8$, separates from dilute alcohol in crystals which decompose without melting at 260° . The pinacone precipitates silver oxide from silver nitrate solution. With mercuric chloride, the hydrochloride of the pinacone yields a *mercurichloride* separating in aggregates of thin needles which soften at 240° and melt at 247° .
T. H. P.

Alkaloids of Mandragora Roots. By OSWALD HESSE (*J. pr. Chem.*, 1901, [ii], 64, 274—286. Compare Thoms and Wentzel, this vol., i, 405).—The author has investigated the alkaloids accompanying hyoscyamine in mandragora roots, using the method of extraction which Wentzel employed. The solution of the alkaloids in sulphuric acid is neutralised with sodium hydrogen carbonate and then extracted with chloroform. The alkaloid thus obtained is shown to be a

hyoscine of the formula $C_{17}H_{21}O_4N$, and not of the formula $C_{17}H_{23}O_3N$, as found by Wentzel. On hydrolysis, the hyoscine yields tropic acid and oscine, $C_8H_{13}O_2N$.

The hyoscine was accompanied by a small quantity of ψ -hyoscyamine, and of a new alkaloid, *mandragorine*. This base was separated from the mother liquor, from which the ψ -hyoscyamine had been extracted, by addition of sodium carbonate and chloroform; the *aurichloride*, $C_{15}H_{19}NO_2 \cdot HAuCl_4$, forms a crystalline powder melting at $124-126^\circ$; hydrolysis with barium hydroxide yields atropic acid and a base resembling tropine.

K. J. P. O.

Preparation of Morpholine from Ethylene by means of the Mercury Ethyl Ether Salt. By JULIUS SAND (*Ber.*, 1901, 34, 2906-2910).—The constitution previously ascribed to the di-iodoethyl ether (*Ber.*, 1901, 34, 1391), namely, $O(CH_2 \cdot CH_2I)_2$, is confirmed by the fact that when the ether is condensed with *p*-toluenesulphonamide (Marckwald, *Abstr.*, 1899, i, 289), and then hydrolysed with 25 per cent. hydrochloric acid at 170° , *p*-toluenesulphonic acid and morpholine hydrochloride (Marckwald and Chain, this vol., i, 380) are formed.

p-Toluenesulphomorpholinamide, $C_6H_4Me \cdot SO_2 \cdot N < \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} > O$, crystallises from alcohol in long, glistening prisms melting at 147° .

Ammonia itself does not convert the di-iodoethyl ether into morpholine, but yields a *tertiary* base, the *picrate* of which melts at 123° .

J. J. S.

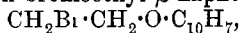
Morpholine. WILHELM MARCKWALD & MICHAEL CHAIN (D.R.-P. 119785).—*Nitrosophenylmorpholine*, obtained by treating a concentrated hydrochloric acid solution of phenylmorpholine with sodium nitrite and decomposing the precipitated *hydrochloride* with sodium carbonate, crystallises from water in lustrous leaflets melting at 100° .

Dinitrophenylmorpholine results from the action of 33 per cent. nitric acid on phenylmorpholine; it crystallises from alcohol in orange-yellow needles melting at 118° .

These compounds, when boiled with 10 per cent. sodium hydroxide solution, yield morpholine together with *p*-nitrosophenol and 2:4-dinitrophenol respectively.

G. T. M.

Morpholine and its Derivatives. WILHELM MARCKWALD & MICHAEL CHAIN (D.R.-P. 120047).—Sulphonamides, when treated with bromoethyl aryl ethers, $CH_2Br \cdot CH_2 \cdot O \cdot Ar$ (2 mols.), and sodium hydroxide (2 mols.), yield diaryl ethers of the corresponding sulphon-diethanolamides, $R \cdot SO_2 \cdot N(CH_2 \cdot CH_2 \cdot OAr)_2$, and these compounds, when hydrolysed with 25 per cent. hydrochloric acid at 170° , yield morpholine or one of its derivatives. For example, *p*-toluenesulphonamide, when treated with bromoethyl β -naphthyl ether,



gives rise to the di- β -naphthyl ether of *p*-toluenesulphon-diethanolamide, $C_7H_7 \cdot SO_2 \cdot N(CH_2 \cdot CH_2 \cdot O \cdot C_{10}H_7)_2$, and this product (m. p. 130°), when hydrolysed, yields morpholine, β -naphthol, toluene, and sulphuric acid. Morpholine is also obtained from *p*-toluenesulphonaminoethyl phenyl ether, $C_7H_7 \cdot SO_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot OPh$ (m. p. 104°), by

condensing this with ethylene chlorohydrin and hydrolysing the product, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{SO}_2\cdot\text{C}_7\text{H}_7)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh}$ (m. p. 73°), with 25 per cent. hydrochloric acid.

Methylmorpholine may be prepared from methyliminoethyl phenyl ether, $\text{NMe}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh})_2$, this compound being obtained, together with methylaminoethyl phenyl ether, $\text{NHMe}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh})$, by the action of bromoethyl phenyl ether on a dilute alcoholic solution of methylamine. The secondary base is removed as a nitrosoamine, whilst the tertiary base is hydrolysed at 160° , yielding methylmorpholine hydrochloride. G. T. M.

Preparation of Morphenol. By EDUARD VONGERICHTEN (*Ber.*, 1901, **34**, 2722—2723).—The conversion of β -methylmorphimethine methiodide into morphenol (Abstr., 1900, i, 248) is best effected by heating with alcoholic potassium hydroxide in sealed tubes at 160° . Similar treatment of the dihydro-compound (Abstr., 1899, i, 551) gives trimethylamine and a compound free from nitrogen, whereas morphine and codeine have been shown to give methylethylamine, and codeine methiodide gives dimethylethylamine (Skraup and Wiegmann, Abstr., 1889, 1018; 1890, 179). T. M. L.

Alkaloids of the Papaveraceæ. By ERNST SCHMIDT (*Arch. Pharm.*, 1901, **239**, 395—408).—An introduction to the following four papers (compare also Henschke, Abstr., 1889, 62; Selle, Abstr., 1890, 649; 1891, 229; Koenig and Tietz, Abstr., 1893, i, 490). The presence of sanguinarine in the root of *Chelidonium majus* was ascertained with certainty by isolating this alkaloid from the residues obtained in the preparation of chelidonine on the large scale.

Protopine has now been prepared by pupils of the author from *Chelidonium majus*, *Stylophoron diphyllum*, *Sanguinaria canadensis*, *Eschscholtzia californica*, and *Glaucium luteum*, and shown in all cases to have the formula $\text{C}_{20}\text{H}_{19}\text{O}_5\text{N}$. The same alkaloid has been isolated by others from *Papaver somniferum*, *Macleaya cordata*, and *Bocconia frutescens*, and consequently has some claim to be regarded as the typical alkaloid of the *Papaveraceæ*. Moreover, it has just been isolated from *Fumaria officinalis* by Trowbridge in the author's laboratory, and probably it is this substance which has been described under different names as occurring in various other plants allied with the *Papaveraceæ*. It forms monoclinic crystals [$a : b : c = 0.8992 : 1 : ?$; $\beta = 57^\circ 19'$].

β - and γ -Homochelidonine appear to be physical isomerides, with the formula $\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}$. α -Homochelidonine, on the other hand, appears to have a different formula, $\text{C}_{21}\text{H}_{21}\text{O}_5\text{N}$.

Glaucine, it is pointed out, may be a lower homologue of corydaline. Its physiological action (which is described) is similar to that of other *Papaveraceæ* alkaloids, but has characteristics of its own. C. F. B.

Alkaloids of Sanguinaria Canadensis. By RICHARD FISCHER (*Arch. Pharm.*, 1901, **239**, 409—420).—Chelerythrine, sanguinarine, homochelidonine, and protopine were isolated from the roots of *Sanguinaria canadensis*; the method employed is detailed in the paper. Chelerythrine turns yellow in air containing carbon dioxide. When

crystallised from solvents containing alcohol it melts at 203° and has the composition $C_{21}H_{17}O_4N, EtOH$ (Schmidt, Koenig, and Tietz, Abstr., 1893, i, 490). When crystallised from toluene, however, it melts at 257° and has the composition $2C_{21}H_{17}O_4N, H_2O, C_6H_5Me$; the toluene is lost at 100° , but the water not even at 140° .

The sanguinarine obtained melted at 211° and had the composition $2C_{20}H_{15}O_4N, EtOH$.

The homochelidonine was obtained in two forms, β and γ , melting at 159° and 169° respectively; the latter crystallises from alcohol and ethyl acetate respectively with the composition $2C_{21}H_{23}O_5N + EtOH$, or $+ EtOAc$. These forms appear to be physical isomerides; each can be converted into the other readily by the employment of a suitable precipitant, temperature, or solvent.

The protopine melted at $206-207^{\circ}$, had the composition $C_{20}H_{19}O_5N$, and crystallographically also was identical with a specimen prepared from *Chelidonium majus*.
C. F. B.

Alkaloids of Eschscholtzia Californica. By RICHARD FISCHER (*Arch. Pharm.*, 1901, 239, 421-425).—All parts of the plant were worked up together, with the result that protopine and β - (or γ -) homochelidonine were isolated, identical with the substances obtained from *Sanguinaria*. Traces of chelerythrine and sanguinarine were probably obtained also. The method employed is described in detail.

C. F. B.

Alkaloids of Glaucium Luteum. By RICHARD FISCHER (*Arch. Pharm.*, 1901, 239, 426-437).—The stem, leaves, and flowers of this plant were worked up together and found to contain protopine, identical with that from *Sanguinaria* and *Eschscholtzia*, and glaucine. In the root protopine was found, and probably traces of chelerythrine and sanguinarine. No homochelidonine was detected in either case. The method employed is described in detail.

Glaucine has been described already by Probst, but evidently his substance was still quite impure. It has the composition $C_{17}H_{13}N(OMe)_4$; it crystallises, although not readily, from ethereal solution in rhombic prisms [$a : b : c = 0.5797 : 1 : 0.2718$], melts at $119-120^{\circ}$, and has $[\alpha]_D + 113.3^{\circ}$ in 5 per cent. alcoholic solution. It is not very stable in air and sunlight, undergoing oxidation readily. It is a very weak base; the *hydrochloride*, with $1HCl$ and $3H_2O$, and *hydrobromide*, with $1HBr$, were analysed. It reacts like a tertiary base with 1 mol. of methyl iodide, forming a *methiodide* which is not decomposed by alkalis; this compound melts at 216° . When it is heated with hydriodic acid, glaucine reacts as though it contained four methoxyl groups; crystals are formed which melt at $225-235^{\circ}$, readily undergo oxidation, and have the composition $C_{17}H_{13}N(OH)_4, HI$.
C. F. B.

Alkaloids of Chelidonium Majus. By M. WINTGEN (*Arch. Pharm.*, 1901, 239, 438-451).—A commercial sample of chelidonine was recrystallised from chloroform-alcohol and then found to have the melting point $135-136^{\circ}$ and the composition $OH \cdot C_{20}H_{18}O_4N, H_2O$. The *phosphate*, with $1H_3PO_4$, and *hydriodide*, with $1HI$, were analysed; the latter is colourless when pure, but soon turns yellow in air and sunlight.

The acetyl derivative melted at 161° ; its *aurichloride* and *platinichloride* are amorphous and melt at 155° and 204° respectively. The benzoyl derivative melted at $210-211^{\circ}$. Attempts to reduce chelidonine with sodium amalgam or with sodium and boiling alcohol, or to oxidise it with barium permanganate in alkaline solution, had negative results. Bromine converts it, in the presence of water, into a *perbromide*, $C_{20}H_{18}O_5NBr.HBr.Br_2$, which is reduced in alcoholic solution by sodium amalgam, or by zinc powder and dilute sulphuric acid, or by hydrogen sulphide, to *bromochelidonine*, $C_{20}H_{18}O_5NBr$. This melts at $225-230^{\circ}$ and forms an amorphous *platinichloride* and *aurichloride* melting at 231° and $137-138^{\circ}$ respectively. When a solution of chelidonine in dilute sulphuric acid is allowed to remain with hydrogen peroxide, crystals of a *peroxide*, $C_{20}H_{18}O_6N.H_2O$, are formed; this substance is reduced by sulphurous acid and by nascent hydrogen, but it does not liberate iodine from a solution of potassium iodide; with gold chloride solution, it yields the aurichloride of chelidonine. In 2 per cent. solution in 96 per cent. alcohol, chelidonine has $[a]_D^{25} 115^{\circ}24'$; in 1 per cent. solution, $150^{\circ}59'$; in 2 per cent. chloroform solution, $117^{\circ}21'$. The sulphate, in 2 per cent. aqueous solution, has $[a]_D^{25} 90^{\circ}56'$.

Protopine, $C_{20}H_{19}O_5N$, and chelerythrine, $C_{20}H_{17}O_4N.EtOH$, were prepared from residues obtained in the commercial preparation of chelidonine, and separated by means of their different solubility in ethyl acetate. The protopine melted at 207° ; its crystalline aurichloride, with $HAuCl_4$, and platinichloride, with $\frac{1}{2}H_2PtCl_6.H_2O$, were analysed.

The chelerythrine melted at $203-204^{\circ}$; its brownish-yellow, amorphous aurichloride, with $HAuCl_4$, and yellow, crystalline platinichloride, with $\frac{1}{2}H_2PtCl_6$, and sulphate, with $H_2SO_4.2H_2O$, were analysed.

From residues of similar origin homochelidonine was obtained in two forms. One, γ , crystallised from alcohol, melted at $169-170^{\circ}$, effloresced readily, and formed monoclinic crystals

$$[a:b:c=0.9883:1:1.4035; \beta=76^{\circ}8'].$$

The other, β , also formed monoclinic crystals, but melted at 160° , and did not effloresce. Both yield the same blood-red, crystalline aurichloride, with $HAuCl_4$, melting at 187° , and yellow, amorphous platinichloride, with $\frac{1}{2}H_2PtCl_6$, containing some water in addition.

C. F. B.

Conversion of Tropidine into Tropine. By RICHARD WILLSTÄTTER (*Ber.*, 1901, **34**, 3163—3165).—The hydrogen bromide additive

compound of tropidine is a 3-bromotropan, $\begin{array}{c} CH_2 \cdot \overset{\text{CH}}{\overset{|}{\text{C}}} \cdot CH_2 \\ | \quad \quad | \\ NMe \quad CHBr \\ | \quad \quad | \\ CH_2 \cdot \overset{\text{CH}}{\overset{|}{\text{C}}} \cdot CH_2 \end{array}$ for on

reduction its methiodide yields exclusively tropan methiodide, and thus differs from 2-bromotropan which gives Δ^3 -methyltropan (this vol., i, 223). The author failed to replace the bromine atom by hydroxyl, either directly by using silver oxide or alkalis, or, indirectly, by means of silver acetate, alkali acetates, or ammonia; in all cases, tropidine or amorphous products were formed. By heating the bromotropan, however, with 10 per cent. sulphuric acid for 3 hours at $200-210^{\circ}$, a mixture of tropidine and ψ -tropine was obtained; as

ψ -tropine is readily transformed into tropine (Abstr., 1900, i, 404), the complete synthesis of atropine and other solanaceous alkaloids has been realised.
W. A. D.

Production of Pyrrolidine-2-carboxylic Acid and of Phenylalanine by the Hydrolysis of Egg-Albumin. By EMIL FISCHER (*Zeit. physiol. Chem.*, 1901, 33, 412—416).—Egg-albumin has been treated in exactly the same manner as casein (this vol., p. 780). The products of hydrolysis were esterified and fractionally distilled. Pyrrolidine-2-carboxylic acid was isolated from the fraction boiling at 90—110° under 25 mm. pressure, and phenylalanine from that boiling at 145—165° under 25 mm. pressure.

The same products may be obtained from gelatin.

J. J. S.

Action of Aminosulphonic Acid on Piperidine. By CARL PAAL and M. HUBALECK (*Ber.*, 1901, 34, 2757—2763. Compare this vol., i, 693).—On heating piperidine aminosulphonate with excess of the base at 150—200°, a piperidinesulphonic acid is obtained in which the group SO_3H is attached to a carbon atom; the intermediate compound in which the sulphonic group is attached to the nitrogen atom could not be isolated.

Piperidine aminosulphonate, $\text{C}_5\text{NH}_{11}\cdot\text{NH}_2\cdot\text{SO}_3\text{H}$, prepared by adding aminosulphonic acid to an alcoholic solution of piperidine, crystallises in white, hygroscopic leaflets melting at 62°.

Piperidine-C-sulphonic acid, $\text{C}_5\text{NH}_{10}\cdot\text{SO}_3\text{H}$, prepared by heating this salt with piperidine under pressure at 180°, crystallises in long, white, spear-like forms which melt at 187—188°. The *potassium* salt is a pale yellow powder; the *barium* salt, with H_2O , and the *silver* salt crystallise in leaflets. Oxidation of the sulphonic acid with silver acetate produced pyridine and sulphuric acid. On distilling the sulphonic acid with potassium hydroxide, a tetrahydropyridine is formed; it is probably the Δ^3 -derivative, as it appears not to be identical with Δ^5 -tetrahydropyridine, prepared by Wolfenstein (Abstr., 1892, 1484), and the acid is therefore the 3- or the 4-piperidinesulphonic acid. The *aurichloride* of the base is a crystalline powder melting and decomposing at 141—142°, and the *benzoyl* derivative a pale yellow oil.

Piperidine-1-sulphonic acid can be prepared by treating an ethereal solution of piperidine with sulphur trioxide; the *barium* salt is a crystalline powder which is decomposed immediately by hydrochloric acid into barium sulphate and piperidine. The free N-sulphonic acid cannot be isolated, as in aqueous solution it is rapidly transformed into the C-sulphonic acid just described.

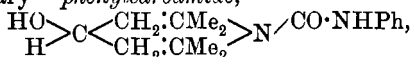
K. J. P. O.

Isomerism in the Piperidine Series. By ERICH GROSCHUFF (*Ber.*, 1901, 34, 2974—2978. Compare Marcuse and Wolfenstein, this vol., i, 608).— α -Vinylidiacetonealkamine [4-hydroxy-2:2:6:6-tetramethylpiperidine] on treatment with phenylcarbimide gives rise to two isomeric products which are considered to be stereoisomeric carbamides.

The "primary" 4-hydroxy-2:2:6:6-tetramethylpiperidylphenyl-carbamide, $\text{HO}\cdot\text{C}\begin{smallmatrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{H} \end{smallmatrix} > \text{N}\cdot\text{CO}\cdot\text{NHPh}$, produced from its generators in a hot benzene solution, crystallises from this solvent in

needles melting at 136° ; its *hydrochloride* melts at 254° and is decomposed by water.

The "secondary" *phenylcarbamide*,



obtained by heating a benzene solution of its isomeride for 40 hours, melts at 147° ; it is seven times as soluble in benzene as the primary compound, but dissolves to the same extent in other solvents; its *hydrochloride* melts at 237° . This isomeride, when heated with concentrated hydrochloric acid at 110° , regenerates the original base. Since these compounds are both very feebly basic, the alternative formula, $\text{NHPh} \cdot \text{CO} \cdot \text{O} \cdot \text{CH} \begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe}_2 \end{array} \text{NH}$, is excluded; neither is the tautomeric structure, $\text{OH} \cdot \text{CH} \begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe}_2 \end{array} \text{N} \cdot \text{C}(\text{OH}) \cdot \text{NPh}$, admissible, for the isomerides do not dissolve in solutions of the alkali hydroxides.

The corresponding *phenylcarbamides* of triacetonealkamine melt respectively at 129° and 138° .
G. T. M.

Synthesis of 2:6-Piperidinedicarboxylic Acids. By EMIL FISCHER (*Ber.*, 1901, **34**, 2543—2549).—Ethyl dibromopimelate, $\text{CH}_2(\text{CH}_2 \cdot \text{CHBr} \cdot \text{CO}_2\text{Et})_2$ (Willstätter, *Abstr.*, 1895, i, 338), was sealed up with liquid ammonia in a pressure tube (cooled with liquid air during the operation) and allowed to remain several days at the ordinary temperature; the tube was then opened (while cooled as before) and the contents evaporated. The residue was a mixture of an amide with the hydrobromide of an isomeric amide. It was extracted with a small quantity of cold water, and the residue crystallised from a little hot water; in this way α -2:6-piperidinedicarboxylamide was obtained in amount equal to 17 per cent. of the original ester. It crystallises with $1\text{H}_2\text{O}$, melts at 228 — 229° (corr.) whether dehydrated or not, and forms a *hydrobromide*, with 1HBr , which melts and decomposes at about 290° . When boiled with excess of aqueous barium hydroxide, it is hydrolysed to α -2:6-piperidinedicarboxylic acid; this melts and decomposes at 258° (corr.), crystallises with $1\text{H}_2\text{O}$, and forms a blue, crystalline *copper* salt which is only slightly soluble in cold water, and so may be utilised in the isolation of the acid.

On concentration, the mother liquor of the amide just described yielded crystals in amount equal to 15 per cent. of the original ester. These were recrystallised repeatedly from small quantities of boiling water, and were then found to melt and decompose at 280° and to contain 1HBr . This *hydrobromide* was decomposed with silver oxide, when β -2:6-piperidinedicarboxylamide was obtained in yield equal to 73 per cent. of the theoretical; it melts at 225 — 226° (corr.). The corresponding β -2:6-piperidinedicarboxylic acid was prepared from the hydrobromide, in yield equal to 93 per cent. of the theoretical, by successive treatment with aqueous barium hydroxide, carbon dioxide, silver sulphate, hydrogen sulphide, and barium hydroxide; it melts at 281° (corr.).

These two acids, $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \\ \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \end{array} \text{NH}$, and their amides are

doubtless stereoisomeric, one pair being *cis*-, and the other *cis trans*-forms (compare Besthorn, Abstr., 1896, i, 252). C. F. B.

3-Nitrosopyrroles. By FRANCESCO ANGELICO and E. CALVELLO (*Gazzetta*, 1901, 31, ii, 4—14. Compare Spica and Angelico, Abstr., 1899, i, 938, and Angeli and Angelico, this vol., i, 45).—By the action of amyl nitrite on the pyrroles in presence of sodium ethoxide, the sodium salts of the corresponding nitroso-derivatives are formed; these salts are less soluble in water than those of the nitrosoindoles (*loc. cit.*) and their solutions have a more intense yellow colour. The action of carbon dioxide on the salts yields the nitrosopyrroles which react readily with acetic anhydride, benzoyl chloride, &c.

4-Nitroso-2:3:5-triphenylpyrrole, $N \begin{smallmatrix} \swarrow \text{CPh} \cdot \text{C} \cdot \text{NOH} \\ \searrow \text{CPh} \cdot \text{CPh} \end{smallmatrix}$, obtained by gradually adding amyl nitrite (1 mol.) to a mixture of sodium ethoxide (1 mol.) and 2:3:5-triphenylpyrrole (1 mol.), separates from benzene in sparkling, yellowish-brown scales, or from alcohol in shining golden-yellow needles melting and decomposing at 197—199°. It combines with phenylcarbimide, whilst the sodium salt reacts readily with ethyl iodide or benzoyl chloride and gives yellowish or reddish precipitates with silver nitrate, ferric, barium, or platinum chloride, copper sulphate, or uranium acetate. The *ethyl* ester, $C_{22}H_{15}N \cdot NOEt$, prepared from the nitroso-compound by the action of sodium ethoxide and ethyl iodide, crystallises from light petroleum in reddish-brown needles melting at 125°. The *benzoyl* derivative, $C_{29}H_{20}O_2N_2$, crystallises from alcohol in dark red needles melting at 189°. With phenylcarbimide, the nitroso-derivative gives the compound $C_{22}H_{15}N \cdot N \cdot O \cdot CO \cdot NHPh$, which separates from benzene in dark red needles melting at 142°.

3-Nitroso-2:5-diphenylpyrrole, $N \begin{smallmatrix} \swarrow \text{CPh} \cdot \text{C} \cdot \text{NOH} \\ \searrow \text{CPh} \cdot \text{CH} \end{smallmatrix}$, prepared from 2:5-diphenylpyrrole and amyl nitrite in presence of sodium ethoxide, crystallises from benzene or xylene in small, shining, maroon needles melting and decomposing at 204°. With phenylcarbimide, it yields a compound which forms a brownish-grey powder melting at 193—194°.

3-Nitroso-5-phenyl-2-methylpyrrole, $N \begin{smallmatrix} \swarrow \text{CMe} \cdot \text{C} \cdot \text{NOH} \\ \searrow \text{CPh} \cdot \text{CH} \end{smallmatrix}$, prepared from the corresponding phenylmethylpyrrole, is obtained by the action of carbon dioxide on a solution of the sodium salt as a yellowish-brown powder which becomes intensely brown at 160° and black at 240°, at which temperature it is still unmelted; it is soluble in alkalis and combines with phenylcarbimide. T. H. P.

A Characteristic Fission of the Pyrrole Ring. By PAUL DUDEN and D. HEYNSIUS (*Ber.*, 1901, 34, 3054—3062. Compare Abstr., 1900, i, 671—674).—*α*-2-Methylcamphenapyrrole-3-carboxylic acid, obtained on hydrolysing its ethyl ester with a dilute alcoholic solution of sodium hydroxide, crystallises from alcohol in prisms melting at 246°; its hydrochloric acid solution gives a slight pyrrole reaction, and the acid itself, when warmed with 40 per cent. sulphuric acid, changes into the isomeric *β*-acid. These isomerides are distinguished

from each other by their different solubilities in ether, this solvent dissolving 60 parts of the β -acid but only 0.5 part of the α -compound.

α -2-Methylcamphenepyrrole, $\begin{array}{c} \text{CH}_2 \diagup \text{CMe} \diagdown \text{C} \cdot \text{CH} \\ | \quad | \quad | \\ \text{CH}_2 \diagdown \text{CMe}_2 \diagup \text{C} \cdot \text{NH} \end{array} \gg \text{CMe}$, prepared by

distilling the preceding compound under diminished pressure, is a very unstable crystalline substance, rapidly becoming red; it melts at 65° and is readily soluble in all the organic solvents excepting light petroleum. The *picrate* melts at 116° .

This base, which has an odour resembling that of hydrocyanic acid, is decomposed by dilute sulphuric acid, yielding a γ -diketone,

acetonylisocamphor, $\begin{array}{c} \text{CH}_2 \diagup \text{CMe} \diagdown \text{CH} \cdot \text{CH}_2 \text{Ac} \\ | \quad | \quad | \\ \text{CH}_2 \diagdown \text{CMe}_2 \diagup \text{CO} \\ | \\ \text{CH} \end{array}$, an oil boiling at $290-291^\circ$

and having n_D 1.485 at 22° and a sp. gr. 1.029 at $22^\circ/4^\circ$. The *disemicarbazone*, a microcrystalline powder, melts at 215° ; the *phenylhydrazone* crystallises in leaflets melting at $128-129^\circ$, and the *p-bromophenylhydrazone* in prisms melting at $154-156^\circ$. The *imide*, $\text{C}_{13}\text{H}_{21}\text{ON}$ (compare this vol., i, 163), formed from the diketone by the action of alcoholic ammonia, crystallises in needles and melts at 151° ; it sublimes in woolly needles and is decomposed into its generators on boiling with alcohol or water. α -2-Methylcamphenepyrrole yields on reduction equal parts of the diketone and *methylcamphenepyrroline*,

$\begin{array}{c} \text{CH}_2 \diagup \text{CMe} \diagdown \text{C} \cdot \text{CH} \cdot \text{CMe} \cdot \text{NH} \\ | \quad | \quad | \\ \text{CH}_2 \diagdown \text{CMe}_2 \diagup \text{CH} \end{array}$, a pale yellow oil boiling at $246-248^\circ$;

the *picrate* and *platinichloride* melt at 200° and 210° respectively.

β -2-Methylcamphenepyrrole is now considered to have the formula $\begin{array}{c} \text{CH} \cdot \text{CMe} \text{---} \text{C} \cdot \text{CH} \\ | \quad | \quad | \\ \text{CH}_2 \cdot \text{CHPr}^a \cdot \text{C} \cdot \text{NH} \end{array} \gg \text{CMe}$, and when prepared from sodium β -methylcamphenepyrrolecarboxylate it is accompanied by a solid isomeride, γ -2-methylcamphenepyrrole, the two products being separated by fractional crystallisation from light petroleum. The new compound melts at 43° , and closely resembles the β -isomeride in chemical properties; both substances give a well-marked pyrrole reaction and do not lose ammonia when treated with dilute sulphuric acid. G. T. M.

Chloro-derivatives of the Pyridine Bases. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 116386. Compare D.R.-P. 109933).—The alkyl and aryl chlorocarbonates interact with pyridine, yielding compounds of the type $\text{OR} \cdot \text{C}_5\text{NH}_5 \cdot \text{CO} \cdot \text{C}_5\text{NH}_5\text{Cl}$. These substances, when treated with alcohols or phenols, decompose, giving rise to a mixture of pyridine hydrochloride, pyridine, and the corresponding mixed carbonate, $\text{RO} \cdot \text{CO} \cdot \text{OR}'$. The following compounds,

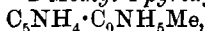
$\text{OEt} \cdot \text{C}_5\text{NH}_5 \cdot \text{CO} \cdot \text{C}_5\text{NH}_5\text{Cl}$,
 $\text{OMe} \cdot \text{C}_6\text{NH}_4\text{Me} \cdot \text{CO} \cdot \text{C}_5\text{NH}_4\text{MeCl}$, and
 $\text{OPh} \cdot \text{C}_5\text{NH}_3\text{Me}_2 \cdot \text{CO} \cdot \text{C}_5\text{NH}_3\text{Me}_2\text{Cl}$,

are described; they are unstable, hygroscopic, yellow substances, and are rapidly decomposed by water.

G. T. M.

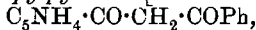
Resolution of an Optically Inactive Base by an Active Alkyl Haloid. By MAX SCHOLTZ (*Ber.*, 1901, 34, 3015—3020).—The product of the action of active amyl iodide ($[\alpha]_D + 4.50^\circ$) on 1-methyl-2-pipecoline at 100° consists of a mixture of crystalline and syrupy quaternary iodides. These substances, when heated at 200° with aqueous ammonia, lose methyl iodide and become converted into the same 1-amyl-2-pipecoline. It follows from this that the optically active iodide combines equally readily with both the optically active constituents of 1-methyl-2-pipecoline, and does not effect any resolution of this racemic base. The solid 1-methyl-2-pipecoline amyliodide crystallises in prisms, melts at 214° , and has $[\alpha]_D + 4.4^\circ$ at 20° ; the corresponding *platinichloride*, $(C_{12}H_{26}N)_2PtCl_6$, and *aurichloride* crystallise in needles melting respectively at 239 — 240° and 140 — 141° . 1-amyl-2-pipecoline boils at 200 — 202° under 750 mm. pressure; it has a sp. gr. 0.8302 at 20° and $[\alpha]_D + 2.77^\circ$ to 3.04° at 20° ; its *platinichloride* crystallises in pyramids melting at 196° ; the *aurichloride* forms leaflets melting at 142° .
G. T. M.

Condensations of the Ester of *iso*Nicotinic Acid. By RUDOLF TSCHERNE (*Monatsh.*, 1901, 22, 615—626. Compare Micko, *Abstr.*, 1897, i, 96, and Ferenczy, *Abstr.*, 1898, i, 271).—4- α -*Diketobutylpyridine* [4-aceto-acetylpyridine], $C_5NH_4 \cdot CO \cdot CH_2Ac$, is prepared by dropping an ethereal solution of ethyl *isonicotinate* and acetone on to alcohol-free sodium ethoxide; the product of the reaction is treated with water and carbon dioxide and extracted with benzene; it crystallises in colourless needles melting at 62° , and boils at 145 — 147° under 18 mm. pressure. The alcoholic solution gives a dark red coloration with ferric chloride. Boiling concentrated potassium hydroxide slowly decomposes it into acetone and *isonicotinic acid*. The *platinichloride*, forms reddish-brown, lustrous leaflets decomposing at 228° ; the methiodide, golden-yellow needles. The *mono-oxime*, $C_5NH_4 \cdot CO \cdot CH_2 \cdot CMe \cdot N \cdot OH$, forms colourless, lustrous crystals melting at 164 — 165° . When the alcoholic solution of 4-acetoacetylpyridine is boiled with aniline hydrochloride, an *anilide*, $C_5NH_4 \cdot CO \cdot CH_2 \cdot CMe \cdot NPh$, is obtained, crystallising in yellow leaflets which melt at 103 — 104° ; dilute alkalis and acids bring about the elimination of aniline. 2-Methyl-4-pyridylquinoline,



prepared when the anilide is heated with concentrated sulphuric acid, forms white crystals melting at 101 — 102° .

4- α -*Diketo- γ phenylpropylpyridine* [4-benzoacetylpyridine],



prepared from ethyl *isonicotinate* and acetophenone, crystallises in colourless needles melting at 80° , and boils at 233° under 18 mm. pressure: the alcoholic solution gives a deep red colour with ferric chloride. The *hydrochloride* crystallises in greenish-yellow needles with a silky lustre; the *platinichloride* forms a dark yellow, crystalline powder. With hydroxylamine, an oxime is not formed, but when an alcoholic solution of 4-benzoacetylpyridine is boiled with hydroxylamine hydrochloride, an *isooxazole* derivative is formed

which has the constitution $C_5NH_4 \cdot C \begin{smallmatrix} \diagup CH \cdot CPh \\ \diagdown N-O \end{smallmatrix}$ or

$$C_5NH_4 \cdot C \begin{smallmatrix} \diagup CH \cdot CPh \\ \diagdown O-N \end{smallmatrix};$$

it crystallises in white leaflets, with a silvery lustre, melts at 165° , and is not decomposed by boiling with potassium hydroxide or dilute acids. K. J. P. O.

Ester-Formation with Pyridinepolycarboxylic Acids. By HANS MEYER (*Monatsh.*, 1901, 22, 577—586. Compare this vol., i, 407).—Methyl hydrogen phthalate yields, with thionyl chloride, the chloride $COCl \cdot C_6H_4 \cdot CO_2Me$, which is a colourless oil decomposing at 100° into phthalic anhydride and methyl chloride. With methyl alcohol, it gives dimethyl phthalate, and with ethyl alcohol, *methyl ethyl phthalate*; the latter is a colourless oil boiling at $285-287^\circ$. With thionyl chloride, ethyl hydrogen phthalate similarly yields an acid chloride (compare Zelinsky, *Abstr.*, 1887, 669).

2-Methyl quinolinate 3-chloride, $(COCl \cdot C_5NH_3 \cdot CO_2Me)$, prepared by warming 2-methyl 3-hydrogen quinolinate with thionyl chloride, crystallises in colourless needles melting and decomposing at 126° ; with methyl alcohol, it gives the *hydrochloride* of the dimethyl ester as colourless hygroscopic needles melting at 56° . *2-Methyl 3-ethyl quinolinate* is formed when the methyl ester chloride is treated with ethyl alcohol; it is a colourless oil boiling and decomposing at $250-255^\circ$; the hydrochloride is hygroscopic; the *platinichloride* forms orange red crystals melting and decomposing at 165° . *2-Ethyl quinolinate 3-chloride* melts at 163° , and with methyl alcohol gives *3-methyl 2-ethyl quinolinate*, an oil which boils and decomposes at $254-258^\circ$; the *platinichloride* crystallises in straw-yellow needles melting at 174° .

Methyl cinchomeronate chloride, $COCl \cdot C_5NH_3 \cdot CO_2Me$, prepared from methyl hydrogen cinchomeronate, crystallises in silky needles melting and decomposing at 183° ; with methyl alcohol, it gives the hydrochloride of the dimethyl ester, and with ammonia the diamide.

Pyridine-2:3:4-tricarboxylic acid reacts only slowly with thionyl chloride; the product yields, with methyl alcohol, the hydrochloride of a dimethyl ester. Dimethyl pyridine-2:3:4-tricarboxylate readily gives a crystalline chloride, which with methyl alcohol produces *trimethyl pyridine-2:3:4-tricarboxylate*, $C_5NH_2(CO_2Me)_3$; the latter compound crystallises in lustrous needles melting at 97° ; the *hydrochloride* forms hygroscopic needles melting at 68° . *Triethyl pyridine-2:3:4-tricarboxylate*, prepared in a similar manner from the diethyl ester, is an oil boiling and decomposing at $300-305^\circ$; the hydrochloride crystallises in long, lustrous needles melting at 61° .

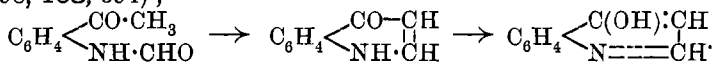
K. J. P. O.

Chloriodohydroxyquinoline. BASLER CHEMISCHE FABRIK (D.R.-P. 117767).—*Chloriodohydroxyquinoline*, is prepared by digesting a potassium hydroxide solution of 5-chloro-8-hydroxyquinoline with

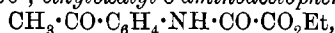
a solution of iodine in potassium iodide or a mixture of this salt with a hypochlorite; it crystallises from glacial acetic acid in yellowish-brown needles, melts at 177—178°, and is very sparingly soluble in water or alcohol.

G. T. M.

Conversion of Aminophenylpropionic Acid into Kynurenic Acid and Allied Compounds. By RUDOLF CAMPS (*Ber.*, 1901, **34**, 2703—2718; *Zeit. physiol. Chem.*, 1901, **33**, 390—411).—*Formyl-o-aminoacetophenone*, $\text{CHO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_3$, prepared by boiling *o*-aminoacetophenone with formic acid during 5 or 10 minutes only, crystallises from hot alcohol in minute, colourless, glistening needles and melts at 79°. It is readily hydrolysed by boiling with hydrochloric acid, but when boiled with sodium hydroxide is converted into 4-hydroxyquinoline, which was found to be identical with the kynurin first prepared by Schmiedeberg and Schulzen (*Annalen*, 1872, **164**, 155) by heating Liebig's kynurenic acid (*Annalen*, 1853, **86**, 125 1858, 108, 354);



o-Aminoacetophenone (2 mols.) combines at the ordinary temperature with ethyl oxalate (1 mol.) to form an *additive* product, $\text{C}_{22}\text{H}_{28}\text{O}_6\text{N}$, which crystallises from light petroleum in pale yellowish, glistening needles, melts at 42°, and is decomposed by acids. When heated together at 150—160°, *ethyl oxalyl-o-aminoacetophenone*,



results, and by crystallising from hot alcohol is obtained in glistening needles melting at 128°. Under the action of sodium hydroxide, the oxalyl compound condenses to a 4-hydroxyquinoline-2-carboxylic acid,

$\text{C}_6\text{H}_4 \begin{array}{l} \text{C}(\text{OH})\cdot\text{CH} \\ \diagdown \quad || \\ \text{N}=\text{C}\cdot\text{CO}_2\text{H} \end{array}$ which crystallises from dilute acetic acid in silky, felted needles, melts with liberation of carbon dioxide at 290°, and is converted into kynurin; the acid is isomeric with kynurenic acid, which must therefore be the 3-acid.

Ethyl formyl-o-aminophenylpropionate, $\text{CHO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{C}\cdot\text{CO}_2\text{Et}$, prepared by the action of formic acid on ethyl *o*-aminophenylpropionate dissolved in ether, crystallises from alcohol in stout, colourless, silky needles, melts at 83°, and when boiled with sodium hydroxide in aqueous alcoholic solution is converted into kynurenic acid.

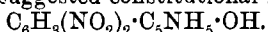
Ethyl acetyl-o-aminophenylpropionate, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{C}\cdot\text{CO}_2\text{Et}$, crystallises in minute needles, melts at 124°, and is converted by alkalis into 2-hydroxy-4-methylquinoline, a substance melting at 228°, and 4-hydroxyquinoline-3-carboxylic acid.

T. M. L.

Preparation of 2:4-Dihydroxyquinoline. BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 117167).—A quantitative yield of 2:4-dihydroxyquinoline (γ -hydroxycarbostyryl) is obtained when an alkali, calcium, or barium salt of acetylanthranilic acid is heated at 280—300° with dry potassium hydroxide or a mixture of this reagent and quicklime (compare D.R.P. 102894).

G. T. M.

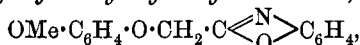
α -Dinitrophenylpyridine Chloride and the Product of its Transformation under the Influence of Alkali. By LEOPOLD SPIEGEL (*Ber.*, 1901, **34**, 3021—3024. Compare Abstr., 1900, i, 51).—[With KATZENELLENBOGEN.]—This investigation, although still incomplete, affords additional evidence in support of the author's view regarding the constitution of the product, $C_{11}H_9N_3O_5$, obtained from α -dinitrophenylpyridine chloride by the action of alkalis. This substance, when heated for some time with absolute alcohol, decomposes into pyridine and 2:4-dinitrophenyl ethyl ether; this behaviour is in accordance with the suggested constitutional formula,



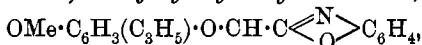
G. T. M.

Condensation Products of Phenoxyacetic Acids with *o*-Aminophenol. By GEORG COHN (*J. pr. Chem.*, 1901, [ii], **64**, 293—296. Compare this vol., i, 352).—Phenoxyacetic acid and its derivatives condense with *o*-aminophenol at 170° to form highly coloured products, from which 1-phenoxyethylbenzoxazoles can be isolated. These substances readily dissolve in alkalis, the oxazole nucleus being broken and phenoxyacetaminophenols produced. Acids precipitate the benzoxazole from the alkaline solution; if the alkaline solution is boiled, the last mentioned compounds are resolved into *o*-aminophenol and the phenoxyacetic acid.

1-Phenoxyethylbenzoxazole, $OPh \cdot CH_2 \cdot C \begin{smallmatrix} \diagup N \\ \diagdown O \end{smallmatrix} C_6H_4$, crystallises in needles and melts at 146—147°; 1-*p*-tolylloxymethylbenzoxazole $C_6H_4Me \cdot O \cdot CH_2 \cdot C \begin{smallmatrix} \diagup N \\ \diagdown O \end{smallmatrix} C_6H_4$, melts at 142°—143°; 1-*thymylloxymethylbenzoxazole*, $C_6H_3MePr \cdot O \cdot CH_2 \cdot C \begin{smallmatrix} \diagup N \\ \diagdown O \end{smallmatrix} C_6H_4$, crystallises in needles melting at 191—192°; the *carvacryloxy*-compound forms leaflets melting at 195—197°; 1-*guaiacyloxymethylbenzoxazole*,



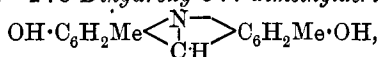
melts at 143—144°; 1-*eugenylloxymethylbenzoxazole*,



crystallises in long needles melting at 111—113°.

α -Naphthylloxymethylbenzoxazole, $C_{10}H_7 \cdot O \cdot CH_2 \cdot C \begin{smallmatrix} \diagup N \\ \diagdown O \end{smallmatrix} C_6H_4$, melts at 220°, and the β -naphthyl derivative at 204°. K. J. P. O.

2:8-Dihydroxy-3:7-dimethylacridine. LEOPOLD CASSELLA (*D.R.-P.* 120466).—2:8-Dihydroxy-3:7-dimethylacridine,



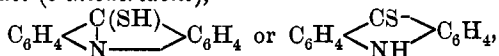
produced by condensing 4-amino-*o*-cresol with formaldehyde in the presence of dilute sulphuric acid, separates from water in orange-coloured crystals; it is slightly soluble in dilute acids, but readily dissolves in alkalis to an orange-yellow solution having an intense green fluorescence. G. T. M.

Thioacridone. KALLE & Co. (*D.R.-P.* 120586).—Thioacridone,

$C_6H_4 \begin{smallmatrix} \diagup CS \\ \diagdown NH \end{smallmatrix} C_6H_4$, prepared by fusing acridine with sulphur at 200° , melts at 271° , and dissolves in concentrated hydrochloric acid, yielding a crystalline hydrochloride. G. T. M.

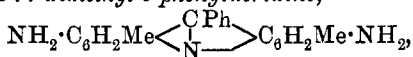
Acridine. I. By ALBERT EDINGER and W. ARNOLD (*J. pr. Chem.*, 1901, [ii], 64, 182—198. Compare this vol., i, 166).—On heating acridine with sulphur monochloride under pressure at 270 — 280° , a compound, $C_{13}HNC_6S_2$, is formed; it crystallises in deep red, insoluble needles melting at 306° and is of neutral character.

5-Thioacridol (5-thioacridone),



is produced when flowers of sulphur and acridine are heated under pressure at 190 — 195° and forms reddish-brown crystals melting at 275° ; it also crystallises, with H_2O , in brownish-yellow needles and dissolves both in alkalis and acids, but not in solutions of carbonates; the hydrochloride crystallises in greenish-yellow needles, which rapidly lose hydrogen chloride. 5-Thioacridol is readily benzoylated by the Schotten-Baumann method and forms a benzyl thioether with benzyl chloride, which by alcoholic hydrogen chloride is converted into acridone and benzyl mercaptan; with methyl iodide, a methyl thioether is obtained; oxidising agents produce acridone. From the solution of thioacridol in dilute nitric acid, ammonia precipitates a strongly basic substance containing sulphur; if the solution in nitric acid is heated, sulphuric acid and a mixture of acridone and nitrated acridone are formed. K. J. P. O.

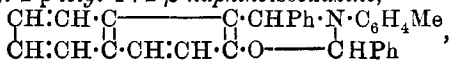
Preparation of Acridine Colouring Matters by means of Benzaldehyde. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 118075).—2:8-Diamino-3:7-dimethyl-5-phenylacridine,



prepared by heating at 120 — 160° benzylidene-2:4-tolylenediamine with a mixture of *p*-toluidine and its hydrochloride, is a brown powder sparingly soluble in water. G. T. M.

Condensation between β -Naphthol, Aldehydes, and Amines. III. By MARIO BETTI (*Gazzetta*, 1901, 31, ii, 170—184. Compare this vol., i, 81 and 611).—The main bulk of the product obtained by the interaction of β -naphthol with an amine and an aldehyde, consists of an oxazine derivative, but a secondary product is also formed, which, in the case of benzylamine, has been separated in quantity sufficient to allow of its properties being studied. The latter compound is formed from 1 mol. each of β -naphthol, aldehyde, and base, with the elimination of $1H_2O$; it gives a diacetyl derivative, and is perfectly analogous to the additive products obtained from aldehydoaminic bases and naphthols (compare Betti, this vol., i, 81).

1:3-Diphenyl-2-*p*-tolyl-4:2- β -naphthoisoaxazine,



prepared from β -naphthol, benzaldehyde, and *p*-toluidine, separates from a mixture of benzene and light petroleum as a white, crystalline powder, which begins to turn yellow at 190° and melts at 205° ; with ferric chloride solution, it gives no colour in the cold, but on warming, the liquid becomes intensely reddish-violet

1 : 3-Diphenyl-2-benzyl-4 : 2- β -naphthoisoosoxazine, $C_{31}H_{25}ON$, obtained from β -naphthol, benzaldehyde, and benzylamine, is deposited from a mixture of benzene and light petroleum as a white, crystalline powder melting at 187° . It is not changed by cold ferric chloride solution, but on heating the liquid assumes a ruby-red coloration, which disappears on cooling. It forms an *acetyl* compound, $C_{31}H_{24}ONAc$, which separates in rosettes of small, white crystals melting at 190° ; with ferric chloride, it behaves like the parent substance.

Benzylidene-benzylamine- β -naphthol, $CH_2Ph \cdot NH \cdot CHPh \cdot C_{10}H_6 \cdot OH$, also obtained from β -naphthol, benzaldehyde, and benzylamine, crystallises from 90 per cent. alcohol in large, shining needles melting at 145° . With cold ferric chloride solution, it gives a dark violet coloration. Its *diacetyl* derivative, $C_{25}H_{25}O_3N$, is deposited from alcohol in yellow, spherical, crystalline aggregates melting at 166° ; with ferric chloride solution, it gives no coloration, even on boiling. It reacts with benzaldehyde, giving 1 : 3-diphenyl-2-benzyl-4 : 2- β -naphthoisoosoxazine.

The interaction of β -naphthol, benzaldehyde, and amylamine gives rise to :

(1) 1 : 3-Diphenyl-2-amyl-4 : 2- β -naphthoisoosoxazine, $C_{29}H_{29}ON$, which separates from alcohol in small, rhomboidal crystals; these melt at 141° and with ferric chloride solution give, on warming, a reddish-violet coloration which disappears on cooling.

(2) *Benzylidene-amylamine- β -naphthol*, $C_6H_{11} \cdot NH \cdot CHPh \cdot C_{10}H_6 \cdot OH$, which crystallises from alcohol in long, white needles melting at 120° ; with ferric chloride solution, it gives, in the cold, an intense dark violet coloration.

1 : 3-Diphenyl-2-ethyl-4 : 2- β -naphthoisoosoxazine, $C_{26}H_{23}ON$, obtained by the interaction of β -naphthol, benzaldehyde, and ethylamine, crystallises from alcohol in hard, sparkling scales melting at 146° and on heating with ferric chloride solution gives a red coloration.

1 : 3-Diphenyl-2-methyl-4 : 2- β -naphthoisoosoxazine, $C_{25}H_{21}ON$, prepared from β -naphthol, benzaldehyde, and methylamine, crystallises from alcohol in yellowish needles melting at 137° ; with ferric chloride solution, it gives a red coloration only on heating. T. H. P.

Two New Nitroaminodiphenylamines. By FREIDRICH KEHRMANN and G. STEINER (*Ber.*, 1901, **34**, 3089—3092).—When heated for 7 hours at 170 — 180° , *o*-chloronitrobenzene condenses with *m*-phenylenediamine, forming 2-nitro-3'-aminodiphenylamine, which crystallises in long red needles from alcohol, melts at 112° , and forms a *sulphate* crystallising in yellow needles or prisms; the corresponding 2 : 3'-diaminodiphenylamine, obtained by the reduction of the nitro-compound, forms a colourless *hydrochloride*, which crystallises in concentric groups of needles.

2-Nitro-2'-aminodiphenylamine, obtained in small quantities along

with diaminophenazine and fluorindine by the condensation of *o*-chloro-nitrobenzene and *o*-phenylenediamine, crystallises in yellowish-red needles and melts at 103°.

R. H. P.

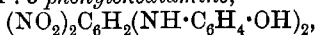
Nitro-*m*-phenylenediaminesulphonic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 120345).—1 : 3-Dichloro-6-nitrobenzene-4-sulphonic acid, prepared by sulphonating *m*-dichlorobenzene with fuming sulphuric acid (23 per cent. SO₃) and nitrating the product with a mixture of this acid and concentrated nitric acid, separates out from the mixture on the addition of water in pale yellow needles. 6-Nitro-1 : 3-phenylenediamine-4-sulphonic acid, obtained by heating the dichloro-compound with 30 per cent. ammonia solution at 150°, crystallises from water in yellow, silky needles sparingly soluble in hydrochloric acid. The lead and potassium salts crystallise in yellow needles.

G. T. M.

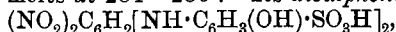
Di-*p*-substituted Diphenylamine Derivatives with free Ortho-positions. FARBERWERKE VORM. MEISTER, LUCIUS, & BRUNING (D.R.-P. 117891. Compare D.R.-P. 112180).—*p*-Amino-*p*-hydroxyphenyl-*m*-tolylamine, NH₂·C₆H₄·NH·C₆H₃Me·OH, is readily prepared by condensing *p*-nitrobenzenesulphonic acid with *p*-aminocresol, reducing the product, and heating the resulting aminosulphonic acid, NH₂·C₆H₃(SO₃H)·NH·C₆H₃Me·OH, with 60 per cent. sulphuric acid; it crystallises in white needles melting at 166°.

G. T. M.

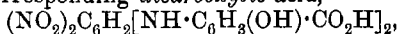
***p*-Dihydroxydiphenyl-4 : 6-dinitro-1 : 3-phenylenediamine.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 121211).—*p*-Dihydroxydiphenyl-4 : 6-dinitro-1 : 3-phenylenediamine,



produced by heating 1 : 3-dichloro-4 : 6-dinitrobenzene (1 mol.) and *p*-aminophenol (2 mols.) with sodium acetate and alcohol, crystallises in red plates and melts at 284—286°. Its disulphonic acid,



obtained by substituting for *p*-aminophenol its sulphonic acid, forms yellowish-red crystals soluble in water and precipitated by sodium chloride. The corresponding dicarboxylic acid,



prepared from aminosalicic acid and 1 : 3-dichloro-4 : 6-dinitrobenzene, is a yellow powder insoluble in water and only slightly soluble in alcohol, benzene, or glacial acetic acid.

G. T. M.

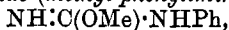
Oxygen Ethers of the Carbamides. Methyl- and Ethyl-isocarbamide. By RALPH H. MCKEE (*Amer. Chem. J.*, 1901, 26, 209—264. Compare Stieglitz and McKee, *Abstr.*, 1899, i, 594; 1900, i, 340, 431).—Phenylethylisocarbamide (ethyl iminophenylcarbamate), NH₂·C(OEt)·NPh or NH·C(OEt)·NHPH, obtained by passing dry hydrogen chloride into a well-cooled alcoholic solution of phenylcyanamide, is a colourless liquid of amine-like odour, which boils at 138—139.5° under 18 mm. pressure, does not solidify at -15°, has *n*_D 1.5575 at 23°, and is readily soluble in the usual organic solvents; it dissolves sparingly in water, forming a strongly alkaline solution. It is not affected by exposure to the air or by boiling water, but if heated with water in a sealed tube it is slowly decomposed. When

heated with hydrogen chloride, it yields ethyl chloride and phenylcarbamide. The *hydrochloride* crystallises from water in groups of long needles and melts and decomposes at 110° . The *platinichloride* forms dark yellow plates and melts and decomposes at 160° .

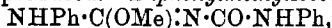
Phenylguanidine does not possess the properties ascribed to it by Feuerlein (Abstr., 1880, 44). By heating a mixture of cyanamide, aniline hydrochloride, and alcohol in a sealed tube for $2\frac{1}{2}$ hours at 100° , it is obtained as a hygroscopic, crystalline solid, which melts at 66° , absorbs carbon dioxide from the air, and undergoes decomposition when strongly heated in a vacuum. The *platinichloride* melts and decomposes at $197-198^{\circ}$. The *dibenzoyl* derivative crystallises in needles and melts at 183.5° . The picrate melts at 221° .

By the action of aniline on phenylethylisocarbamide at 175° in a sealed tube, phenylcarbamide, ethylaniline, and ethylamine are produced. When an ethereal solution of phenylethylisocarbamide is treated with benzoyl chloride, an oily mixture of two isomeric *benzoyl* derivatives is obtained, which slowly deposits slender prisms; when this oily mixture is heated with hydrochloric acid, ethyl chloride, benzoyl-phenylcarbamide, and benzanilide are formed.

Phenylmethylisocarbamide (methyl phenyliminocarbamate),

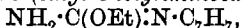


obtained by the action of hydrogen chloride on a solution of phenylcyanamide in methyl alcohol, boils at 124° under 10 mm., 133° under 15 mm., and 140° under 23 mm. pressure; it forms a crystalline solid which melts at 46.5° and has a fishy odour and bitter taste. If it is heated with dilute hydrochloric acid, ethyl chloride and phenylcarbamide are produced. The *hydrochloride* melts and decomposes at 90° . The *sulphate* crystallises in plates and melts at 139° . By the action of benzoyl chloride on phenylmethylisocarbamide, two isomeric compounds are produced. The *s-benzoyl* derivative, $\text{NHBz}\cdot\text{C}(\text{OMe})\cdot\text{NPh}$, is obtained as an oil which is decomposed by hydrogen chloride with formation of methyl chloride and *s-benzoylphenylcarbamide*; it yields salts with both bases and acids. The *as-benzoyl* derivative, $\text{NBzPh}\cdot\text{C}(\text{OMe})\cdot\text{NH}$, is a crystalline solid which melts at $64-65^{\circ}$, and, like the *s*-derivative, forms potassium and silver salts; when heated with dry hydrogen chloride, methyl chloride is evolved and crystals of *as-benzoylphenylcarbamide* melting at 146° are produced. *Diphenylmethylisobiuret,*



obtained by the action of phenylcarbimide on phenylmethylisocarbamide, is a crystalline substance which melts at 111° and is soluble in chloroform, alcohol or ether; when the *hydrochloride* is heated in a vacuum, methyl chloride and α -diphenylbiuret are produced.

o-Tolyethylisocarbamide (ethyl o-tolyliminocarbamate),



obtained by the action of hydrogen chloride on an alcoholic solution of *o*-tolylcyanamide, boils at 144° under 19 mm. pressure and has not been solidified; it is decomposed by dry hydrogen chloride with formation of ethyl chloride and *o*-tolylcarbamide melting at 190° . The *platinichloride* crystallises in hexagonal prisms and melts and decomposes at 177° .

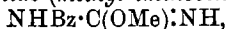
When *as*-phenylmethylisocarbamide is heated with dilute hydro-

chloric acid, ethyl chloride and *as*-phenylmethylcarbamide are produced, together with some methylaniline and methylethylaniline.

α-Diphenyl-*α*-methyllethylisobiuret, $\text{NPhMe}\cdot\text{C}(\text{OEt})\cdot\text{N}\cdot\text{CO}\cdot\text{NHPh}$, obtained by the action of phenylcarbimide on phenylmethylethylisocarbamide, melts at 115—116°, and when boiled with dilute hydrochloric acid yields ethyl chloride and *α*-diphenyl-*α*-methylbiuret melting at 101—102°.

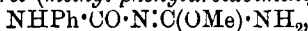
as-Phenyldimethylisocarbamide (methyl iminophenylmethylcarbamate), $\text{NPhMe}\cdot\text{C}(\text{OMe})\cdot\text{NH}$, boils at 120° under 11 mm. pressure.

Benzoylmethylisocarbamide (methyl iminobenzoylcarbamate),



crystallises in monoclinic prisms, melts at 76·5°, and has both basic and acidic properties; when it is heated with dilute hydrochloric acid, methyl chloride, benzoylcarbamide, benzoic acid, and methylamine are produced.

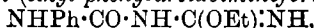
Phenylmethylisobiuret (methyl phenylureidoiminoformate),



obtained by the action of phenylcarbimide on methylisocarbamide, crystallises in four-sided prisms with blunt pyramidal ends and melts at 89·5—90°; the *hydrochloride* melts and decomposes at 133°. When phenylmethylisobiuret is boiled with dilute hydrochloric acid, methyl chloride is evolved and *α*-phenylbiuret, which melts at 156—156·5° and is soluble in alcohol or hot water, is produced.

Ethylisocarbamide *hydrochloride* melts at 123—124°, evolving ethyl chloride. The *platinichloride* crystallises in four-sided, dark yellow plates and melts and decomposes at 178·5°. By the action of dilute hydrochloric acid on ethylisocarbamide, ethyl chloride, carbamide, and a small quantity of ethylurethane are produced.

Phenylethylisobiuret (ethyl phenylureidoiminoformate),

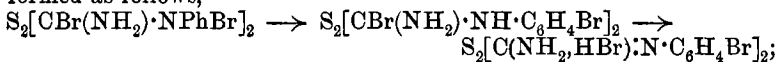


crystallises in monoclinic prisms, melts at 85·5—86°, and when heated with dilute hydrochloric acid yields ethyl chloride and phenylbiuret; the *hydrochloride* melts and decomposes at 141°.

Comparative determinations of the hydrolysis of the hydrochlorides of ethyl iminobenzoate and phenyl ethylisocarbamide show that the former is hydrolysed by water in approximately *N*/12 concentration to the extent of rather less than 1 per cent., whilst the hydrochlorides of phenylethyl- and phenylmethylisocarbamides are not hydrolysed at all at this concentration, and further that whilst ethyl iminobenzoate is a fairly strong base, easily undergoing ionisation, phenylethylisocarbamide is a still stronger base, the affinity constant of which is probably close to that of potassium or sodium hydroxide. E. G.

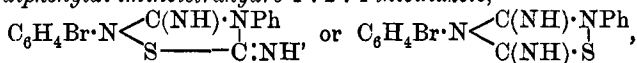
Action of Halogens on Thiocarbamides. By A. HUGERSHOFF (*Ber.*, 1901, **34**, 3130—3135).—Phenylcarbamide in chloroform solution interacts with bromine in its isodynamic form, $\text{SH}\cdot\text{C}(\text{NH}_2)\cdot\text{NPh}$, giving hydrogen bromide and *carbamino*phenyliminodisulphide *tetrabromide* (*bromocarbaminophenylbromoaminodisulphide*), $\text{S}_2[\text{CBr}(\text{NH}_2)\cdot\text{NPhBr}]_2$, which melts and decomposes at about 208°, gradually loses bromine on exposure to the air, and is reduced by sulphurous acid solution to *carbamino*phenyliminodisulphide, $\text{S}_2[\text{C}(\text{NH}_2)\cdot\text{NPh}]_2$; this crystallise

from water in nacreous leaflets, melts at 128° , and yields a well-defined *hydrochloride* melting at 236° and a crystalline *platinichloride*. The tetrabromide dissolves in water, yielding a mixture of carbamino-phenyliminodisulphide and its *bromo-derivative*, $S_2[C(NH_2):N \cdot C_6H_4Br]_2$, formed as follows,



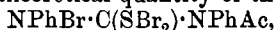
by a transformation common to the bromoamino-bases the *hydrobromide* of the base forms white needles and melts at $261-263^{\circ}$.

In alcoholic solution, phenylthiocarbamide yields with bromine a *bromodiphenyldi-iminotetrahydro-1 : 2 : 4-thiodiazole*,



which melts at 172° and yields a *hydrobromide* crystallising from water and melting at $242-244^{\circ}$. As this compound cannot be obtained by brominating carbaminophenyliminodisulphide in alcohol, the latter is obviously not an intermediate product in the action. W. A. D.

Action of Bromine on Acetyldiphenylthiocarbamide in Chloroform Solution. By A. HUGERSHOFF and W. CHR. KÖNIG (*Ber.*, 1901, **34**, 3136—3142).—The action of bromine on acetyldiphenylthiocarbamide in chloroform solution gives rise to hydrogen bromide and a nearly theoretical quantity of the *bromide*,



which forms orange-coloured crystals, melts and decomposes at 167° , and is converted by aqueous sodium hydroxide or sulphurous acid into the *sulphoxide*, $NPh \cdot C(SO) \cdot NPhAc$; the latter is remarkably stable and is not changed by alkaline lead hydroxide, mercuric oxide, concentrated sulphuric acid, alcoholic potassium hydroxide, or sodium amalgam. Water, unlike dilute alkali, converts the foregoing bromide into the *bromosulphoxide*, $C_6H_4Br \cdot NH \cdot C(SO) \cdot NPhAc$, the bromine of the bromophenylamino-radicle wandering into the phenyl nucleus (compare preceding abstract); the product crystallises from alcohol in small, colourless needles, melts at 165° and is stable towards alkaline lead hydroxide, alkalis, and acids. W. A. D.

Phenacylidenebenzamidine and some Homologues. By FRANZ KUNCKELL and R. BAUER (*Ber.*, 1901, **34**, 3024—3029. Compare this vol., i, 294).—Phenacylidenebenzamidine is a weak base and yields a *hydrochloride*, $NH : CPh : N : CH : CPh \cdot HCl$, and a *sulphate* crystallising in needles and melting respectively at 310° and 193° ; the *platinichloride* forms yellow crystals and decomposes on heating. The *phenylhydrazone*, $NH : CPh : N : CH : CPh : N \cdot NHPh$, melts at 181° ; the *silver derivative*, $Na_2 \cdot CPh : N : CH : CPh$, formed by the interaction of the imino-base with ammoniacal silver nitrate, is a voluminous white precipitate, becoming dark on exposure to light. The *ethiodide*, $C_{17}H_{17}ON_2I$, separates from alcoholic solutions in white crystals melting at 180° .

p-Tolacylidenebenzamidine, $NH : CPh : N : CH : CO \cdot C_6H_4Me$, prepared from benzamidine and *p*-tolyl dibromomethyl ketone, crystallises from alcohol in white leaflets melting at 254° ; the *hydrochloride* melts at 316° and the *phenylhydrazone* at 176° ; the *platinichloride* separates in

small crystals and decomposes without melting. The *silver* derivative is a white, insoluble, flocculent compound, the *ethiodide* forms white crystals melting at 218° ; the latter substance, on treatment with a dilute alcoholic solution of potassium hydroxide, yields the *ethyl* derivative, $\text{NEt}\cdot\text{CPh}\cdot\text{N}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$; this product, which is also obtained by the action of ethyl iodide on the silver derivative, separates in white crystals and melts at 257° .

Phenacylidene-p-tolenylamidine, $\text{NH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{N}\cdot\text{CH}\cdot\text{COPh}$, produced by the interaction of *p*-tolenylamidine and dibromoacetophenone in dry ether, forms white crystals melting at 220° ; the *hydrochloride* separates in white needles and melts at 111° .

p-Tolacylidene-p-tolenylamidine, $\text{NH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{N}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$, prepared in a similar manner to the preceding base, melts at 240° .

G. T. M.

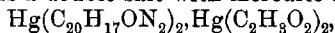
Action of Benzamidine on Certain Aromatic Aldehydes. By FRANZ KUNCKELL and R. BAUER (*Ber.*, 1901, 34, 3029—3032).—

Benzylidenebenzamidine, $\text{NH}\cdot\text{CPh}\cdot\text{N}\cdot\text{CHPh}$, is readily obtained by adding benzaldehyde or benzylidene chloride to benzamidine dissolved in dry chloroform and then heating the mixture on the water-bath for 2—3 hours; it crystallises in colourless needles, melts at 175° , and yields a white, insoluble, *silver* derivative; its *hydrochloride* melts at 274° .

o-Hydroxybenzylidenebenzamidine, $\text{NH}\cdot\text{CPh}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, melts at 185° ; its *hydrochloride* and *platinichloride* melt respectively at 155° and 215° , the *silver* derivative is a white, insoluble compound. Benzoyl-formaldehyde readily interacts with benzamidine, yielding the compound $\text{NH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{COPh}$.

G. T. M.

Hydroxyamidines. By HEINRICH LEY (*Ber.*, 1901, 34, 2620—2631. Compare Abstr., 1898, i, 252).— α,β -Diphenyl- γ -benzylhydroxyamidine, $\text{NPh}\cdot\text{CPh}\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{OH}$ (*loc. cit.*), which melts at 150° , possesses feeble acid properties and also somewhat stronger basic properties. The *hydrochloride* crystallises in sparingly soluble needles and melts and decomposes at 194° . The aqueous solution has an acid reaction and it may be calculated from the electrical conductivity that this salt is hydrolysed in aqueous solution to four times the extent of aniline hydrochloride. The *platinichloride* forms brown, octahedral crystals and the *cobalt* and *nickel* salts are both crystalline. The *mercury* salt, $\text{Hg}(\text{C}_{20}\text{H}_{17}\text{ON}_2)_2$, crystallises in yellow needles and is not decomposed by aqueous sodium hydroxide. It forms a double salt with mercuric acetate,



which crystallises in light yellow needles melting at 142° . From a solution of this salt, sodium hydroxide precipitates only the mercuric oxide corresponding with the mercuric acetate. It seems probable that the metallic compounds belong to two different types, the easily decomposed sodium salt may have the formula $\text{NPh}\cdot\text{CPh}\cdot\text{N}(\text{ONa})\text{C}_7\text{H}_7$, whilst the stable mercury salt probably contains the metal united to

nitrogen, $(\text{C}_7\text{H}_7\cdot\text{N}\text{---}\text{O}\text{---}\text{CPh}\cdot\text{NPh})\text{Hg}$. The alcoholic solution of the amidine gives a blue coloration with ferric chloride and a greenish-black coloration with manganese acetate. The *benzyl ether* crystallises in small needles melting at 99° and gives no coloration with ferric chloride. On one occasion, a second product of benzylation was

obtained which melted at 163° . The *picryl ether*, $C_{28}H_{19}O_7N_5$, is obtained by the action of picryl chloride in alcoholic solution and forms orange-red crystals with a green surface lustre, which melt and decompose suddenly at $130-131^{\circ}$. The chloroform solution exhibits a strong green fluorescence, whilst the alcoholic solution is only faintly fluorescent, and this behaviour appears to be characteristic of the hydroxyamidines. *β -Phenyl- α -o-tolyl- γ -benzylhydroxyamidine* forms a copper salt, $(C_{21}H_{19}ON_2)_2Cu$, which crystallises in bronze coloured plates. *β -Phenyl- α -m-nitrophenyl- γ -benzylhydroxyamidine* crystallises in golden coloured needles melting at 171° and shows all the characteristic reactions. The copper salt forms brownish-red plates, the cobalt salt crystallises in microscopic, brown needles, and the nickel salt is an orange-yellow, crystalline precipitate. *Benzoyl-m-nitroanilideiminochloride*, from which the foregoing hydroxyamidine is prepared, crystallises in tablets melting at $80-82^{\circ}$.

β -Phenyl- γ -benzyl- $\alpha\beta$ -naphthylhydroxyamidine crystallises in yellowish needles melting at 175° and forms characteristic copper and cobalt salts. A. H.

1:7-Diamino-2-hydroxynaphthalene. LEOPOLD CASSELLA & Co. (D.R.-P. 117298).—1:7-Diamino-2-hydroxynaphthalene, prepared by reducing either the azo-compound, obtained by adding benzenediazonium chloride to an alkaline solution of 7-amino- β -naphthol, or the product of the action of nitrous acid on the same amino-compound, crystallises in lustrous leaflets melting at 220° and differs from the diaminonaphthol previously described (Abstr., 1890, 1424) in yielding a violet solution with nitrous acid, whereas the isomeride develops a reddish-brown coloration. G. T. M.

[Diaminodihydroxyanthraquinonesulphonic Acid.] FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117892).—A diaminodihydroxyanthraquinonesulphonic acid having the following constitution, $CH_2:C(NH_2) \cdot \overset{|}{\underset{|}{C}} \cdot CO \cdot \overset{|}{\underset{|}{C}} \cdot C(OH) = \overset{|}{\underset{|}{C}} \cdot SO_3H$, $CH_2:C(OH) \cdot \overset{|}{\underset{|}{C}} \cdot CO \cdot \overset{|}{\underset{|}{C}} \cdot C(NH_2):CH$, is prepared by sulphonating *p*-diaminoanthrarufin (compare Schmidt and Gattermann, Abstr., 1897, i, 197) with fuming sulphuric acid (5 per cent. SO_3) or chlorosulphonic acid; it is obtained as a dark powder sparingly soluble in cold water. The acid yields a well characterised pyridine salt and dyes wool blue either with or without a mordant. G. T. M.

[*p*-Diaminochrysazinsulphonic Acid.] FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117893. Compare preceding abstract).—*p*-Diaminochrysazin, $CH_2:C(OH) \cdot \overset{|}{\underset{|}{C}} \cdot CO \cdot \overset{|}{\underset{|}{C}} \cdot C(OH) = \overset{|}{\underset{|}{C}} \cdot H$, $CH_2:C(NH_2) \cdot \overset{|}{\underset{|}{C}} \cdot CO \cdot \overset{|}{\underset{|}{C}} \cdot C(NH_2):CH$ (compare D.R.-P. 98639 and 100138), yields a monosulphonic acid on treatment with fuming sulphuric acid; this substance dyes wool blue either with or without a mordant (compare Eng. Pat. 7291 of 1900). G. T. M.

The Three Isomeric β -Aminophenylbenziminazoles. By BOL. MIKLASZEWSKI and STEFAN VON NIEMENTOWSKI (*Ber.*, 1901, 34, 2953—2974. Compare Abstr., 1899, i, 643).—The β -aminophenylbenziminazoles are colourless crystalline compounds insoluble in

water, but readily soluble in organic media. They are decided bases, yielding well-defined salts with two equivalents of an acid, the nitrates and hydrochlorides being readily soluble in water or alcohol. The acetyl derivatives of the meta- and para-compounds do not yield cyclic di-anhydrides, and in this respect differ from the ortho-compound. Both acetyl and benzoyl derivatives are indifferent substances and only sparingly soluble in organic solvents. On treatment with alcoholic hydrogen sulphide, the *m*- and *p*-iminoazoles yield thiocarbamide derivatives, which are yellow in colour and soluble in alkalis.

All three iminoazoles may be diazotised in strongly acid solution at 0°, and the diazo-salts thus obtained, when added to alkaline β -naphthol solution, yield characteristic red dyes, and when reduced with stannous chloride, form yellow hydrazines soluble in alkalis and acids, but only sparingly so in organic solvents. These hydrazines reduce ammoniacal silver nitrate but not Fehling's solution, and yield hydrazones with aldehydes, ketones, and ketonic acids.

m-Nitrobenzoyl-*o*-nitroanilide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, forms pale yellow needles melting at 138°, dissolves in concentrated mineral acids, also in alkalis, and unlike the *o*-compound does not change colour on exposure to light. β -*m*-Aminophenylbenziminazole melts at 251–252°; the hydrochloride, $\text{C}_{13}\text{H}_{11}\text{N}_3 \cdot 2\text{HCl}$, forms prismatic crystals melting at 328°, the nitrate, $\text{C}_{13}\text{H}_{11}\text{N}_3 \cdot \text{HNO}_3$, melts and decomposes at 265–270°. The acetyl derivative, $\text{C}_6\text{H}_4 \langle \text{N} \rangle \text{NH} \rangle \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, crystallises from alcohol in short, colourless needles melting at 288° and is only sparingly soluble in acetone, benzene, or toluene. The benzoyl derivative, $\text{C}_{20}\text{H}_{15}\text{ON}_3$, forms compact crystals melting and decomposing at 139°. The thiocarbamide derivative, $\text{C}_{27}\text{H}_{20}\text{N}_6\text{S}$, forms a yellow, amorphous mass. β -Naphthol- β -*m*-azophenylbenziminazole, $\text{C}_{23}\text{H}_{16}\text{ON}_4$, is a bright scarlet-red powder melting at 156–157° and insoluble in water, but soluble in alkalis. The isomeric *o*-compound forms a brick-red powder melting at 272°; this dye is not formed so readily as its two isomerides.

β -*o*-Hydrazinophenylbenziminazole, $\text{C}_6\text{H}_4 \langle \text{N} \rangle \text{NH} \rangle \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH}_2$, crystallises from alcohol in yellow, rhombic plates melting and decomposing at 182° and is only sparingly soluble in ether or water; the hydrochloride, $\text{C}_{13}\text{H}_{12}\text{N}_4 \cdot 2\text{HCl}$, forms yellow, glistening needles melting at 248°, and the nitrate, with 2HNO_3 , dark brown prisms melting and decomposing at 136°. The isomeric *m*-hydrazino-compound forms yellow plates melting between 245° and 258°, the hydrochloride melts at 256–257°, and the nitrate decomposes and melts at 145°.

p-Nitrobenzoyl-*o*-nitroanilide melts at 216°; Kym (this vol., i, 47) gives 219–220° as the melting point. The corresponding benziminazole melts at 240° (235–236° Kym); the hydrochloride, $\text{C}_{13}\text{H}_{11}\text{N}_3 \cdot 2\text{HCl}$, melts and decomposes at 348°, and the nitrate, $\text{C}_{13}\text{H}_{11}\text{N}_3 \cdot \text{HNO}_3$, between 215° and 230°; the acetyl derivative crystallises in short, thick needles melting at 299°; the benzoyl derivative forms rhombic plates or needles melting at 333°; the thiocarbamide, $\text{C}_{27}\text{H}_{20}\text{N}_6\text{S}$, forms crystalline rods melting and decomposing at

236—237°. β -Naphthol- β -p-azophenylbenzimidazole crystallises in red needles melting at 297—298°. β -p-Hydrazinophenylbenzimidazole melts and decomposes at 305°; the hydrochloride, with 2HCl, crystallises in yellow needles melting at 190—191°.

The following hydrazones have been prepared :

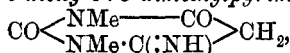
β -Phenylbenzimidazole hydrazone.

| | Ortho. | Meta. | Para. |
|--------------------|---|--|--|
| Benzaldehyde | { melts and decomposes at 180°. | { Yellow crystals, softens at 170°, begins to decompose at 200°. | { Softens at 100°, decomposes at 120° |
| Pyruvic acid | { Decomposes between 120° and 180° | { Stout needles, softens at 184°, melts and decomposes at 195°. | { Yellow needles, softens at 193°, decomposes at 220°. |
| Acetophenone | { Pale yellow prisms, softens at 102°, melts at about 135°. | { Not definitely crystalline, begins to decompose at 180°. | { Yellow, begins to decompose at 148°. |

β -8-Quinolinebenzimidazole (Abstr., 1899, i, 647) forms a hydrochloride, $C_{16}H_{11}N_3 \cdot 2HCl$, which crystallises in pale grey needles melting at 260°. β -5-(or 7-)Quinolinebenzimidazole crystallises, with $1H_2O$, in small needles, softens at 100—105°, and melts at 135—136°; it dissolves readily in most organic solvents and in mineral acids; the hydrochloride, with 2HCl, softens at 229° and melts at 236°, the nitrate with $2HNO_3$, forms long needles melting and decomposing at 196°. β -6-Quinolinebenzimidazole crystallises, with $1H_2O$, in pale grey needles melting at 105°; the anhydrous compound melts at 218°, the hydrochloride melts at 180—181°, and the nitrate melts and decomposes at 223—224°.

J. J. S.

Cyclic Carbamides [Pyrimidines]. WILHELM TRAUBE (D.R.-P. 117922).—Cyanooacetyl methylcarbamide, produced by condensing cyanoacetic acid and methylcarbamide in the presence of phosphorus oxychloride, melts at 205°. Iminomalonylmethylcarbamide (4-imino-2:6-dioxy-1-methylpyrimidine), $CO \begin{smallmatrix} \text{NMe} \text{---} \text{CO} \\ \text{NH} \cdot \text{C}(\text{:NH}) \end{smallmatrix} > CH_2$, a colourless crystalline substance resulting from a rearrangement of the preceding compound under the influence of solutions of the alkali hydroxides, decomposes without melting and yields a purple isonitroso-derivative, $C_6H_8O_3N_4$, on treatment with nitrous acid. Iminomalonyldimethylcarbamide (4-imino-2:6-dioxy-1:3-dimethylpyrimidine),



crystallises from water and yields a purple isonitroso-compound, $C_6H_8O_3N_4$ (compare Mulder, Abstr., 1879, 618).

G. T. M.

4:5-Dimethylpyrimidine. By JULIUS SCHLENKER (Ber., 1901, 34, 2812—2829).—2:6-Dioxy-4:5-dimethylpyrimidine (4:5-dimethyluracil), $NH-CO-NH$, obtained by heating iminodimethyluracil with hydrochloric acid under pressure, crystallises in pointed rods, melts at

290°, can be distilled, and, when treated with phosphorus oxychloride, is converted into the corresponding 2 : 6-dichloro-4 : 5-dimethylpyrimidine, which crystallises in long plates, melts at 70—71°, boils at 249—250°, and dissolves readily in most solvents. 4 : 5-Dimethylpyrimidine,

$\text{N}=\text{CH}=\text{N}$
 $\text{CH}\cdot\text{CMe}\cdot\text{CMe}$, obtained from the dichloro-compound by treatment with zinc dust and water, crystallises in needles melting at 3°, boils at 176.5—177°, has a quinoline-like odour, gives a neutral solution in water, and forms a yellow, crystalline *platinichloride*, $(\text{C}_6\text{H}_5\text{N}_2)_2\text{PtCl}_4$, which melts and decomposes at 242—243°, an *aurichloride*, $\text{C}_6\text{H}_5\text{N}_2\cdot\text{AuCl}_3$, which crystallises in yellow needles and melts and decomposes at 120°, and a *mercurichloride*, $\text{C}_6\text{H}_5\text{N}_2\cdot 2\text{HgCl}_2$, which crystallises in needles and melts at 207°. When 4 : 5-dimethylpyrimidine is oxidised with an aqueous solution of potassium permanganate, a *monocarboxylic acid* (probably 5-methylpyrimidine-4-carboxylic acid) is obtained; this crystallises in compact needles, melts at 190°, forms a *copper salt* which crystallises in rhombs and melts at 259—260°, and when heated above its melting point, yields a *base* (probably 5-methylpyrimidine), which melts at 15° and boils at 142°.

6-Chloro-2-amino-4 : 5-dimethylpyrimidine, obtained by treating imino-dimethyluracil with phosphorus oxychloride, crystallises in pointed rods, melts at 215—216°, dissolves in most warm solvents, and forms a *picrate*, which crystallises in small yellow plates melting at 198°; a *hydrochloride*, in lustrous needles; a *platinichloride*, in yellowish-red needles melting at 250°; and an *aurichloride*, in long needles, melting at 160°. 2-Amino-6-thio-4 : 5-dimethylpyrimidine, obtained by treating the corresponding chloro-compound with potassium hydrogen sulphide, is a crystalline substance which sinters at 240° and finally melts at 270°; it forms a crystalline *aurichloride*, *platinichloride*, and *picrate*. 2-Amino-6-anilino-4 : 5-dimethylpyrimidine, obtained by treating the chloro-compound with aniline, crystallises in compact pyramids melting at 202—203°, and forms a crystalline *hydrochloride*, *aurichloride*, and a *dichromate*. The chloro-compound, when reduced with zinc dust and water, yields 2-amino-4 : 5-dimethylpyrimidine, which separates from aqueous solution in long needles, melts at 214—215°, and forms a *hydrochloride*, which crystallises in pointed needles; a *platinichloride*, in small, reddish-yellow plates melting and decomposing at 227°; an *aurichloride*, $\text{C}_6\text{H}_5\text{N}_3\cdot\text{HAuCl}_4$, in long, yellow needles melting at 112°, a *gold salt*, $\text{C}_6\text{H}_5\text{N}_3\cdot\text{AuCl}_3$, as a red, amorphous powder, melting at 142°; a *ferrocyanide* in yellowish-white plates, and a *picrate* melting at 250°.

The isomeric 2-chloro-6-amino-4 : 5-dimethylpyrimidine, obtained by treating the dichloro-compound with ammonia, crystallises from alcohol in pointed rods, melts at 182—183°, and forms a crystalline *hydrochloride*, *platinichloride*, *dichromate*, and *picrate*. The corresponding 2-thio-derivative crystallises in long needles, decomposes above 300°, and forms a crystalline *hydrochloride*, *platinichloride*, and *picrate*. 6-Amino-2-anilino-4 : 5-dimethylpyrimidine crystallises in pointed scales, melts at 166°, forms a crystalline *hydrochloride*, which in aqueous solution gives crystalline precipitates with solutions of auric and platinic chlorides, potassium dichromate, and ferrocyanide, and picric

acid. 6-Amino-4:5 dimethylpyrimidine crystallises in compact rods, melts at 230°, forms a *hydrochloride* which crystallises in feathery forms and in aqueous solution gives crystalline precipitates with the solutions just mentioned.

6-Hydroxy-4:5-dimethylpyrimidine, obtained by treating the dichloro-compound with hydriodic acid, crystallises from benzene in rhombic plates, melts at 204°, forms a *hydriodide* (which crystallises in yellow prismatic forms, sinters at 200°, and finally melts at 210°) and a crystalline *aurichloride*, *platinichloride*, and *picrate*. 6-Chloro-4:5-dimethylpyrimidine, obtained by treating the hydriodide with phosphorus oxychloride, crystallises in small, colourless rods, melts at 51°, boils at 203°, and forms a crystalline *aurichloride*, *ferrocyanide*, and *picrate*, the corresponding 6-thio-derivative crystallises in prismatic forms, softens at 200°, melts at 265°, and forms a crystalline *hydrochloride*, *aurichloride*, *platinichloride*, *dichromate*, *ferrocyanide*, and *picrate*, and the 6-anilino-derivative crystallises in prismatic forms, melts at 152°, and forms a crystalline *hydrochloride*, *platinichloride*, *aurichloride*, *dichromate*, *ferrocyanide*, and *picrate*.

2:6-Diamino-4:5-dimethylpyrimidine, obtained by the continued treatment of the 2:6-dichloro-compound with ammonia, crystallises in prisms, melts at 192°, and forms a crystalline *hydrochloride* and *platinichloride*, melting at 250°; the corresponding 2:6-dianilino-derivative crystallises in pointed prisms and melts at 133—134°; and the 2:6-dithio-derivative crystallises in long rods and decomposes above 300°. 4:5-Dimethyl-2:6-dimethoxypyrimidine, obtained by treating the dichloro-compound with sodium and methyl alcohol, crystallises in rhombic needles, melts at 39—40°, boils at 229°, and forms a crystalline *platinichloride*, *aurichloride*, and *picrate*. R. H. P.

Synthesis of Alkyl Ketodihydroquinazolines from Anthranilic Acid. By AUGUST H. GOTTHELF (*J. Amer. Chem. Soc.*, 1901, 23, 611—632. Compare Bogert and Gotthelf, *Abstr.*, 1900, i, 412, 608).—When anthranilic acid is heated with propionitrile in a sealed tube, 2-ethyl-4-ketodihydroquinazoline is obtained in a yield amounting to 22½ per cent. of the theoretical; by the addition of propionic anhydride or propionic acid, the yield is increased to about 30 per cent.; some propionylaniline is formed in each case. A mixture of anthranilic acid, acetonitrile, and propionic anhydride furnishes the ethylquinazoline in a yield of 17 per cent.; the corresponding methyl compound is not produced in this reaction. 3-Methyl-2-ethyl-4-ketodihydroquinazoline crystallises in long, colourless needles and melts at 121°. The *hydrochloride* crystallises in needles, and sublimes without melting. The *sulphate* melts at 240—241°, the *picrate* at 191—192°, the *oxalate* at 180—181°, and the *nitrate* and *chromate* melt and decompose at 173—174° and 155° respectively; the *platinichloride* forms a red, crystalline powder.

By the action of butyronitrile on anthranilic acid, 2-propyl-4-ketodihydroquinazoline melting at 199—200° is produced, butyramide also being formed; in presence of butyric anhydride, the yield is increased, whilst with butyric acid the same products are obtained together with some butyrylaniline. When a mixture of anthranilic acid, acetonitrile,

and butyric anhydride is heated, the propylquinazoline is produced together with another substance which is probably the corresponding methylquinazoline. 3-Methyl-2-propyl-4-ketodihydroquinazoline crystallises in long, colourless needles and melts at 77—78°. The *hydrochloride* forms thin plates and sublimes without melting. The *sulphate* melts at 227—228°, the *picrate* at 183—184°, and the *oxalate* at 193—194°; the *nitrate* melts and decomposes at 159—160°, and the *chromate* gradually darkens above 150°. The *platinichloride* forms coarse, red crystals.

When anthranilic acid, isobutyric anhydride, and propionitrile are heated together in a sealed tube, 2-isopropyl-4-ketodihydroquinazoline is produced, but no ethylquinazoline is formed. If acetonitrile is used instead of propionitrile, the same quinazoline is obtained but in smaller yields; it melts at 231—232°, and probably exists in two forms. 3-Methyl-2-isopropyl-4-ketodihydroquinazoline crystallises in long, silky needles and melts at 78—79°. The *hydrochloride* forms rectangular plates; the *sulphate* decomposes on heating, the *picrate* melts at 213—214°; and the *platinichloride* is obtained in coarse, red crystals.

By the action of isovaleronitrile on anthranilic acid, 2-isobutyl-4-ketodihydroquinazoline, $C_6H_4 \begin{smallmatrix} N=C \cdot C_4H_9 \\ | \\ CO \cdot NH \end{smallmatrix}$, is produced in a yield of 5 per cent.; in the presence of isovaleric anhydride, the yield is increased to 35 per cent., isovalerylaniline and isovaleramide being simultaneously formed. It crystallises in small needles, melts at 194—195°, and is readily soluble in alcohol or hot benzene, fairly so in ether or hot water, and very slightly so in cold water. The 3-methyl-2-isobutyl-4-ketodihydroquinazoline forms colourless needles and melts at 68—69°; the *hydrochloride* crystallises in needles; the *sulphate* melts at 228—229°; the *picrate* at 192°, and the *oxalate* at 204—205°; the *nitrate* and *chromate* decompose at 171—172° and 154° respectively. The *platinichloride* forms coarse, brown needles.

When anthranilic acid is heated with isohexonitrile, 2-isoamyl-4-ketodihydroquinazoline, $C_6H_4 \begin{smallmatrix} N=C \cdot C_5H_{11} \\ | \\ CO \cdot NH \end{smallmatrix}$, is obtained in a yield of 18 per cent.; in the presence of isohexoic acid, the yield is increased to 37 per cent., and isohexoylaniline and isohexoamide are simultaneously produced; it crystallises in needles, melts at 184°, and is soluble in ether, alcohol, benzene, or hot water. 3-Methyl-2-isoamyl-4-ketodihydroquinazoline crystallises in small needles and melts at 40—41°. The *hydrochloride* forms fine needles, the *nitrate* decomposes at 160—161°, and the *picrate* melts at 164—165°.

The action of a nitrile on anthranilic acid in presence of the anhydride of a lower acid was investigated, with the following results. Propionitrile and acetic anhydride yield the methylquinazoline. *iso*-Hexonitrile and isobutyric anhydride furnish the isopropylquinazoline with probably some isoamylquinazoline. With isohexonitrile and butyric anhydride, the propylquinazoline is obtained together with another substance which is probably the isoamyl compound.

The action of a nitrile on anthranilic acid in presence of a higher acid was also examined. Acetonitrile and propionic acid yield a

mixture which probably consists of the methyl- and ethyl-quinazolines; butyronitrile and decoic acid furnish the propylquinazoline, and with *isohexonitrile* and decoic acid the *isoamylquinazoline* is produced.

The action of a nitrile on anthranilic acid in presence of a lower acid gave the following results. Acetonitrile and formic acid yield formylanthranilic acid but no quinazoline; a similar result was obtained with propionitrile and formic acid. *isoHexonitrile* and formic acid furnish a small quantity of the *isoamylquinazoline*, together with *isohexoamide* and a substance which is probably 4-ketodihydroquinazoline. *isoHexonitrile* and propionic acid yield the *isoamylquinazoline*.

When anthranilic acid is heated with butyric or *isohexoic* acid, no action takes place, whilst with butyric or *isovaleric* anhydride the corresponding acylanthranilic acids are obtained. *isoValeryl anthranilic acid* crystallises from water in needles and melts at 110—111°.

E. G.

4:4'-Diaminodiphenylamine-3'-sulphonic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 119009).—4:4'-*Diaminodiphenylamine-3'-sulphonic acid*, prepared from 4:4'-diaminodiphenylamine-2:3'-disulphonic acid by boiling the latter with 50 per cent. sulphuric acid, separates from the cooled solution in the form of the sulphate; the free acid forms silvery greyish-blue crystals sparingly soluble in water.

The disulphonic acid employed in this reaction is obtained by condensing chloro-*p*-nitrobenzene-*o*-sulphonic acid with *p*-phenylenediaminesulphonic acid and reducing the resulting nitroamine.

G. T. M.

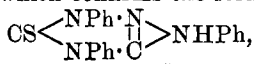
Carbodiphenylimide. By CARL SCHALL (*J. pr. Chem.*, 1901, [ii], 64, 261—273. Compare Abstr., 1900, i, 464).—On melting a mixture of carbodiphenylimide and benzoic acid, a *monobenzoyldiphenylcarbamide*, $\text{NHPh}\cdot\text{CO}\cdot\text{NBzPh}$, is formed; it crystallises in long needles melting at 129°, decomposes into phenylcarbimide and benzanilide on heating, and is probably identical with the compound obtained by Dains (Abstr., 1899, i, 593) from ethyl phenyliminophenylcarbamate and benzoyl chloride.

Carbodiphenylimide can be obtained in a colloidal (γ) form by treating the ordinary form (α) with insufficient benzene to dissolve it. The γ -form is of gelatinous consistency and is reconverted into the ordinary variety by treatment with acetic acid.

On removing sulphur from phenylcyclohexylthiocarbamide by mercuric oxide in the presence of boiling chloroform, an oil is obtained which is probably a reduced carbodiphenylimide; on dissolving the oil in acetic acid, phenylcyclohexylcarbamide (m. p. 180°) separates. From di- α -tetrahydronaphthylthiocarbamide by treatment with α -naphthylamine and lead oxide in alcoholic solution, a derivative of a hydrated carbodi- α -naphthylimide, *α -naphthyl di- α -tetrahydronaphthylguanidine*, $\text{C}_{10}\text{H}_7\cdot\text{N}:\text{C}(\text{NH}\cdot\text{C}_{10}\text{H}_{11})_2$, is obtained; it crystallises in short, microscopic prisms melting at 177—179°.

The author has obtained the triphenylthiotriazolone (m. p. 180°), which is formed from Wessel's dicarbo-base (*loc. cit.*) and carbon

disulphide, by the interaction of anilinodiphenylguanidine and ethyl trithiocarbonate, a fact which confirms the formula,



for the thiotriazolone.

K. J. P. O.

The Fourteenth Isomeride of Rosinduline. By FRIEDRICH KEHRMANN and EMIL OTT (*Ber.*, 1901, **34**, 3092—3098).—4-Amino-1:2-naphthaquinone condenses with 2:3'- and 2:4'-diaminodiphenylamines, forming aminoisorosindulines, from which, by treatment with nitrous acid, the fourteenth and fifteenth isomerides of rosinduline (*isorosindulines*) are obtained.

The *dihydrochloride* of 2:4'-diaminodiphenylamine crystallises in long, colourless prisms and condenses with 4-amino-1:2-naphthaquinone, forming 5:4'-*diaminophenyl- $\alpha\beta$ naphthaphenazonium chloride*; when treated with acetic anhydride, this yields 4'-*acetylaminorosinduline* and 5:4'-*diacetylaminorosinduline*. The *chloride* of the monoacetyl compound crystallises in red laminae with a bronze-like lustre and the *dichromate* is an insoluble, scarlet, crystalline powder. The *chloride* of the diacetyl compound forms orange-yellow, leaf-like crystals with a golden-green iridescence, and the *dichromate* is a red, crystalline powder. The *chloride* of the monoacetyl compound, when treated with nitrous acid, yields *acetylisorosinduline chloride*, which is isolated by means of the additive compound with ferric chloride, forms golden-yellow, leaf-like crystals, and is easily converted into the *dichromate*, which is an insoluble, red powder; this acetyl compound, when treated with sulphuric acid and the resulting solution precipitated with sodium bromide, yields *isorosinduline* (No. 14) (4'-*aminophenyl-naphthaphenazonium bromide*), which is obtained as a reddish-brown, crystalline powder.

R. H. P.

The Fifteenth Isomeride of Rosinduline. By FRIEDRICH KEHRMANN and PAUL NUESCH (*Ber.*, 1901, **34**, 3099—3104).—5:3'-*Diaminophenyl- $\alpha\beta$ -naphthaphenazonium chloride*, obtained by the condensation of 4-amino-1:2-naphthaquinone with the hydrochloride of diaminodiphenylamine, crystallises in aggregates of dark-red needles and was only obtained pure by the hydrolysis of the *diacetyl* derivative, which forms a *chloride* (small, scarlet-red needles with a metallic lustre) and a *dichromate* (red, crystalline precipitate). The *monoacetyl* (3'-*acetyl-amino*-) derivative, obtained when the diamino-chloride reacts with acetic anhydride at the ordinary temperature, forms a *chloride* which shows a yellow and red fluorescence in alcoholic solution and crystallises in green, iridescent aggregates, and a *dichromate*, which was obtained as a deep-red, crystalline precipitate.

Acetylisorosinduline (3'-*acetylaminophenyl- $\alpha\beta$ -naphthaphenazonium chloride*), obtained when the *chloride* of the monoacetyl compound is treated with nitrous acid, is best purified by conversion into the *bromide*, which when hydrolysed with sulphuric acid yields the *bromide* of 3'-*aminophenyl-naphthaphenazonium* (*isorosinduline* No. 15), which is obtained as dark reddish-yellow crystals with a green, metallic lustre; the *dichromate* of the *isorosinduline* crystallises from water in lustrous golden-yellow laminae.

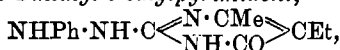
The paper concludes with a comparison of the absorption spectra of

the salts of phenylnaphthaphenazonium and the fourteenth and fifteenth isomerides of *isorosinduline*.
R. H. P.

Preparation of Hydroxytriazoles and their Sulphonic Acids. K. OEHLER (D.R.-P. 119901).—Hydroxytriazoles can be prepared either by fusing the sulphonic acids of the triazoles with sodium hydroxide or by heating the compounds under pressure with a concentrated solution of the alkali.
G. T. M.

Isomeric Anilino-guanidines. By GUIDO PELLIZZARI and CESARE RONCAGLIOLO (*Gazzetta*, 1901, 31, i, 513—526).—2-Phenylhydrazine-4-methylpyrimidone, $\text{NHPh}\cdot\text{NH}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{CMe} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}\text{CH}$, obtained by the condensation of anilino-guanidine and ethyl acetoacetate with elimination of water and alcohol, crystallises from alcohol in minute, white needles which have no definite melting point, but begin to redden at about 200° and decompose at about 230° ; it is slightly soluble in water and exhibits both basic and acid functions. When heated under pressure with moderately concentrated hydrochloric acid, it is completely converted into phenylhydrazine and methyluracil, a reaction which gives its constitution. Its *hydrochloride*, $\text{C}_{11}\text{H}_{12}\text{ON}_4\cdot 2\text{HCl}$, separates in white needles, which redden at 200° , melt and decompose at 220 — 230° and are moderately soluble in alcohol or water. Its *dibromide*, $\text{NHPh}\cdot\text{NH}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{CBrMe} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}\text{CHBr}$, is deposited from acetic acid solution as a white, crystalline powder decomposing at 220 — 222° ; it dissolves in dilute potassium hydroxide but is insoluble in dilute acids.

2-Phenylhydrazine-4-methyl-5-ethylpyrimidone,

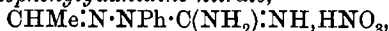


prepared from anilino-guanidine and ethyl ethylacetoacetate, crystallises from alcohol in spherical aggregates of slender needles, which soften at 215° and melt at about 235° .

2-Phenylmethylhydrazine-4-methylpyrimidone, $\text{C}_{12}\text{H}_{14}\text{ON}_4$, prepared from anilinomethylguanidine and ethyl acetoacetate, crystallises from dilute alcohol in long, white needles melting at 192° ; it is soluble in benzene or dilute acids or alkalis and gives a crystalline picrate and platinichloride.

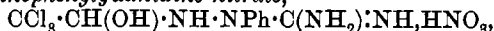
Aminophenylguanidine shows a behaviour quite different from that of its isomeride, as it contains a hydrazine group, by virtue of which it is able to form condensation products with aldehydes and ketones.

Ethylideneaminophenylguanidine nitrate,



obtained by the action of acetaldehyde on aminophenylguanidine nitrate, separates in small, white needles melting at 182° ; it is soluble in water or alcohol and when boiled in acid solution is resolved into its components.

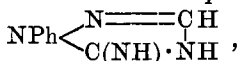
Chloralaminophenylguanidine nitrate,



prepared from chloral and aminophenylguanidine nitrate, is deposited

from aqueous solution in slender, acicular crystals which melt at 130 and are soluble in alcohol.

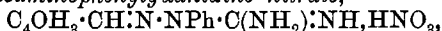
The *ethyl acetoacetate* derivative of *aminophenylguanidine nitrate*, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{N}\cdot\text{NPh}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{HNO}_3$, separates from water in short crystals melting at 160°. 5-*Imino-1-phenyltriazoline*,



obtained by the action of formic acid on aminophenylguanidine, separates in long, shining, white needles melting at 157°; it has basic properties, forming well-defined salts, and is very soluble in alcohol and to a less extent in water or benzene. The *picrate*, $\text{C}_8\text{H}_8\text{N}_4\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises from water in silky, yellow needles melting at 175°, whilst the *platinichloride*, $(\text{C}_8\text{H}_8\text{N}_4)_2\cdot\text{H}_2\text{PtCl}_6$, melts at 197°. T. H. P.

Compounds of Aminophenylguanidine with Aldehydes and Ketones. By GUIDO PELLIZZARI and R. RICKARDS (*Gazzetta*, 1901, 31, i, 526—536).—The possibility of employing aminophenylguanidine as a reagent for the characterisation of aldehydes and ketones has been studied by the authors. With all the aldehydes tried, characteristic compounds were obtained, but this was only the case with a few of the ketones to which the test was applied. The aminophenylguanidine was employed in the form of nitrate, the condensation products obtained being described below.

Furfurylideneaminophenylguanidine nitrate,

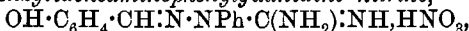


crystallises from alcohol in transparent, colourless prisms which melt and decompose at 171° and dissolve in water and to a less extent in chloroform, benzene, or ether. The corresponding *picrate*,



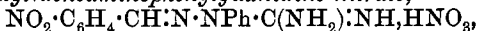
crystallises from alcohol in needles which melt and decompose at 218°. The *platinichloride*, $(\text{C}_{12}\text{H}_{12}\text{ON}_4)_2\cdot\text{H}_2\text{PtCl}_6$, separates in small, orange-yellow crystals melting and decomposing at 207°.

o-Hydroxybenzylideneaminophenylguanidine nitrate,



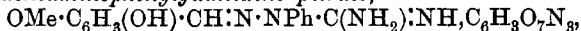
crystallises from alcohol in shining plates which melt and decompose at 207—208° and are moderately soluble in water; under the influence of light, it becomes reddish-yellow. The *picrate*, $\text{C}_{14}\text{H}_{14}\text{ON}_4\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, separates from alcohol in slender, yellow needles which melt and decompose at 254° and are moderately soluble in water. The *platinichloride*, $(\text{C}_{14}\text{H}_{14}\text{ON}_4)_2\cdot\text{H}_2\text{PtCl}_6$, forms orange-yellow needles melting at 220—221° and is slightly soluble in water or alcohol.

m-Nitrobenzylideneaminophenylguanidine nitrate,



crystallises from alcohol in small, white needles which melt and decompose at 199° and are readily soluble in water. The corresponding *picrate* separates from alcohol in golden-yellow needles melting and decomposing at 250° and dissolving slightly in water.

Vanillideneaminophenylguanidine picrate,



crystallises from alcohol in needles which melt and decompose at 234° and are slightly soluble in water.

Citrylideneaminophenylguanidine [*citralaminophenylguanidine*] *nitrate*, $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH} \cdot \text{N} \cdot \text{NPh} \cdot \text{C}(\text{NH}_2) \cdot \text{NH} \cdot \text{HNO}_3$, separates from dilute alcohol in white crystals which soften at 110° and melt completely at about 120° ; it is very soluble in alcohol, benzene, or chloroform and to a less extent in water. The *picrate* crystallises from alcohol in shining, yellow scales melting and decomposing at $166\text{--}170^\circ$ and dissolving slightly in water. The fact that these compounds have indefinite melting points is possibly due to their existence in two isomeric modifications, similar to those obtained by Tiemann in the case of the semicarbazones.

Methylbenzylideneaminophenylguanidine [*acetophenoneaminophenylguanidine*] *nitrate*, $\text{CMePh} \cdot \text{N} \cdot \text{NPh} \cdot \text{C}(\text{NH}_2) \cdot \text{NH} \cdot \text{HNO}_3$, is deposited from alcohol in shining, flattened crystals melting and decomposing at 181° and is slightly soluble in alcohol. The *picrate* separates from alcohol in yellow crystals which melt and decompose at $220\text{--}221^\circ$.

With glyoxal, aminophenylguanidine gives a crystalline compound which was not further investigated; with dextrose, lactose, benzophenone, &c., no condensation products could be obtained.

T. H. P.

3-Alkylxanthine Derivatives. C. F. BOEHRINGER & SONS (D.R.-P. 120437).—Uramil, when condensed with alkyl and aryl thiocarbimides, yields alkylthio- ψ -uric acids; these compounds, when heated with hydrochloric acid, give rise to 3-alkylthiouric acids, which by the action of nitrous acid are transformed into 3-alkylxanthines.

Methylthio- ψ -uric acid, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{CH} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHMe}$, produced from uramil and methyl thiocarbimide in the presence of potassium hydroxide, crystallises in lustrous leaflets with $1\text{H}_2\text{O}$ and melts at 110° . *3-Methylthiouric acid*, $\begin{smallmatrix} \text{NH} \cdot \text{CO} \cdot \text{CH} \cdot \text{N} \\ \text{CO} \cdot \text{NH} \cdot \text{C} \cdot \text{NMe} \end{smallmatrix} \text{C} \cdot \text{SH}$, obtained by heating it with 5 per cent hydrochloric acid, is slightly soluble in water or alcohol and yields an amorphous silver salt. *3-Methylxanthine* is formed from the latter acid by the action of sodium nitrite and hydrochloric acid; it crystallises from water in needles melting at 384° .

3-Phenylthio- ψ -uric acid, a crystalline compound sparingly soluble in alcohol or water, yields successively *3-phenylthiouric acid* and *3-phenylxanthine*, the latter compound crystallising in lustrous leaflets and melting at 337° .

3-Ethylxanthine crystallises in lamellæ, and *3-benzylxanthine* in four-sided plates; these bases melt respectively at 360° and 342° .

G. T. M.

4-Tetrazole. By MARTIN FREUND and TH. PARADIES (*Ber.*, 1901, **34**, 3110—3122).—*Methylthiosemicarbazide hydriodide*, prepared by treating thiosemicarbazide with methyl iodide, is a crystalline soluble salt which sinters at 136° , melts at 140° , and when treated with nitrous acid yields *methylmercaptotetrazole*, $\text{SMe} \cdot \text{C} \begin{smallmatrix} \text{N} - \text{N} \\ \text{NH} \cdot \text{N} \end{smallmatrix}$; this crystallises in rhombic prisms, sinters at 144° , melts and decomposes at 151° ,

forms characteristic *silver* and *copper* salts and, when oxidised with potassium permanganate, yields the corresponding *sulphone*, which crystallises like ice flowers, sinters at 110° , melts at 120° , and forms characteristic *potassium* and *silver* salts.

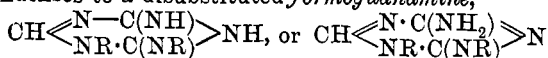
Tetrazolethiol, $\text{SH} \cdot \text{C} \begin{smallmatrix} \text{N} - \text{N} \\ \text{NH} \cdot \text{N} \end{smallmatrix}$, obtained by the action of hydriodic acid on methylmercaptotetrazole, crystallises in white needles melting and decomposing at 205° , forms a *sodium* salt crystallising with $1\frac{1}{2}\text{H}_2\text{O}$, and when treated with dilute nitric acid, yields tetrazole. *Tetrazolesulphonic acid*, obtained by oxidising the thiol with nitric acid, is a syrup; it forms definite *silver*, *lead*, and *barium* salts, and when fused with potassium hydroxide yields *tetrazolol*, $\text{HO} \cdot \text{C} \begin{smallmatrix} \text{N} - \text{N} \\ \text{NH} \cdot \text{N} \end{smallmatrix}$, which crystallises from water, melts at 254° , and forms the *silver* salt, $\text{CN}_4\text{Ag} \cdot \text{OAg}$.

Phenylmercaptotetrazole (from 4-phenylthiosemicarbazide and nitrous acid), when oxidised with chromic acid, yields the *phenyltetrazole*, $\text{HC} \begin{smallmatrix} \text{N} - \text{N} \\ \text{NPh} \cdot \text{N} \end{smallmatrix}$, which melts at $65-66^\circ$, the isomeride

$\text{HC} \begin{smallmatrix} \text{N} \cdot \text{NPh} \\ \text{N} : \text{N} \end{smallmatrix}$ being an oil (see Abstr., 1894, i, 53); this phenyltetrazole forms a *mononitro*-derivative which melts and decomposes at 205° , and when reduced yields the corresponding *amino*-compound which crystallises in silky needles, melts at 155° , and when oxidised yields tetrazole.

These researches support the view that tetrazole is a tautomeric substance, the tautomerism being destroyed by the substitution of the hydrogen atom by a phenyl group. R. H. P.

α -Disubstituted Biguanides and Guanamines. By W. CRAMER (*Ber.*, 1901, 34, 2594—2603).—An alcoholic solution of guanidine, $\text{NH}_2 \cdot \text{C}(\text{NH}) \cdot \text{NH}_2$, is obtained readily by mixing equivalent amounts of guanidine hydrochloride and sodium ethoxide in alcoholic solution, and filtering from the precipitated sodium chloride. When this is mixed with an alcoholic solution of a disubstituted thiocarbamide, $\text{CS}(\text{NHR})_2$, and the whole heated with precipitated mercuric oxide, and filtered from the mercuric sulphide formed, an α -disubstituted (compare Emich, Abstr., 1891, 1180) *biguanide*, $\text{NH}_2 \cdot \text{C}(\text{NH}) \cdot \text{NH} \cdot \text{C}(\text{NR}) \cdot \text{NHR}$, or $\text{C}(\text{NH}_2)_2 : \text{N} \cdot \text{C}(\text{NR}) \cdot \text{NHR}$, a monoacid base with basic properties, crystallises from the filtrate as it cools. If this is digested at 100° with benzoic anhydride in alcoholic solution, it is converted into a *dibenzoyl* derivative. If it is boiled with excess of anhydrous formic acid, it condenses to a disubstituted *formoguanamine*,



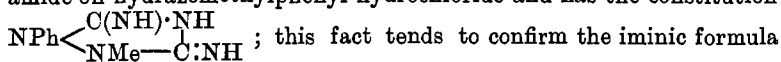
(compare Bamberger and Dieckmann, Abstr., 1892, 736), a monoacid base which can be precipitated from solution by ammonia. If acetic anhydride is used instead of formic acid, the product is the *acetyl* derivative of a disubstituted *acetoguanamine*, $\text{CMe} \begin{smallmatrix} \text{N} \cdot \text{C}(\text{NHAc}) \\ \text{NR} - \text{C}(\text{NR}) \end{smallmatrix} > \text{N}$.

The following substances were prepared; the numbers are melting

points:—*Diphenyl* derivatives ($R = Ph$): *biguanide*, 167° ; *hydrochloride*, $234-235^\circ$; *platinichloride*, nitrate, 216° (not 321° , Bamberger, Abstr., 1881, 43); *dibenzoyl* derivative, yellow, 162° . *Formoguanamine*, yellowish, 206° ; *platinichloride*, yellow. *Acetylacetoguanamine*, yellowish, 217° .—*Di-o-tolyl* derivatives ($R = C_6H_4Me$): *biguanide*, 178° ; *hydrochloride*, 245° . *Formoguanamine*, 255° . *Acetylacetoguanamine*, 191° .—*Di-p-tolyl* derivatives ($R = C_6H_4Me$): *biguanide*, 140° , crystallised with $1EtOH$, 90° ; *nitrate*, 218° . *Formoguanamine*, 222° .—*Di-1:2:4-xylyl* derivatives ($R = C_6H_8Me_2$, the *dithiocarbamide* melts at 152°): *biguanide*, oily; *hydrochloride*, crystalline; *nitrate*, 203° .

Several disubstituted biguanides with different substituting groups were also prepared. *α -Phenylethylbiguanide* melts at $131-132^\circ$. By treating guanyphenylthiocarbamide with silver nitrate in the presence of 1:2:4-xylylidine or *o*-anisidine, there were obtained respectively 1:2:4-xylylphenylbiguanide, paste; *nitrate*, 204° ; and *o*-anisylphenylbiguanide, paste; *nitrate*, 206° . C. F. B.

Researches on Guanazole. By GUIDO PELLIZZARI and CESARE RONCAGLIOLO (*Gazzetta*, 1901, 31, i, 477-513. Compare Abstr., 1892, 356, and 1894, i, 517).—The following derivatives of phenylguanazole (*loc. cit.*) have been prepared:—*Acetylphenylguanazole*, $C_{10}H_{11}ON_5$, crystallises from water in elongated, flat prisms containing $1H_2O$ and melts at 244° ; it is moderately soluble in alcohol, is hydrolysed readily by bases or acids, and loses its water of crystallisation in the air, the crystals becoming opaque. *Diacetylphenylguanazole*, $C_{12}H_{13}O_2N_5$, separates from alcohol in small, white crystals, from water in transparent, white prisms melting at 212° , and from very dilute acetic acid in silky needles containing $4H_2O$; on boiling with dilute hydrochloric acid, it loses acetic acid, yielding phenylguanazole hydrochloride. *Tetra-acetylphenylguanazole*, $C_{16}H_{17}O_4N_5$, obtained by boiling the diacetyl compound in a reflux apparatus with acetic anhydride, separates on the addition of a little alcohol in small needles which melt at 157° and when crystallised from water lose two acetyl residues, giving the preceding compound. Phenylguanazole hence contains 4 replaceable hydrogen atoms. *Benzylidenephénylguanazole*, $C_{15}H_{15}N_5$, obtained by the action of benzaldehyde on phenylguanazole, separates from alcohol in crystals melting at 228° and is slightly soluble in ether, benzene, or chloroform; dilute mineral acids decompose it in the cold, giving benzaldehyde and the corresponding salt of phenylguanazole. *Nitrosophénylguanazole*, $C_8H_8ON_6$, is an orange-yellow, unstable powder which melts at 247° and with sulphuric acid and phenol gives Liebermann's reaction. With methyl iodide, phenylguanazole gives the hydriodide of the phenylmethylguanazole which has been already obtained (*loc. cit.*) by the action of dicyanodiamide on hydrazomethylphenyl hydrochloride and has the constitution



for phenylguanazole. Phenylguanazole platinichloride (*loc. cit.*) does not lose hydrogen chloride when boiled with water, a fact explained by the absence in the nucleus of double bonds.

Iminourazole, $\text{NH} \begin{smallmatrix} \text{CO-NH} \\ \text{NH} \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$, which represents an intermediate compound between urazole and guanazole, is obtained either by the interaction of dicyanodiamidine hydrochloride on hydrazine monohydrochloride or by the action of carbamide on aminoguanidine hydrochloride. It separates from very dilute acetic acid in small, white, acicular crystals melting at 285° , shows slight acid and basic properties, reduces ammoniacal silver nitrate, and gives a red coloration with ferric chloride. *Diacetyliminourazole*, $\text{C}_6\text{H}_5\text{O}_3\text{N}_4$, crystallises from alcohol in small, silky needles melting at above 300° ; its probable constitution is $\text{NAc} \begin{smallmatrix} \text{CO-NH} \\ \text{NAc} \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$. *Phenyliminourazole*,

$\text{NPh} \begin{smallmatrix} \text{CO-NH} \\ \text{NH} \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$, obtained (1) by the action of carbamide on phenylaminoguanidine hydrochloride, (2) by the interaction of dicyanodiamidine and phenylhydrazine, or (3) by heating phenylguanazole with potassium hydroxide solution in an autoclave, separates from water in small, shining, acicular crystals melting at 272° ; it exhibits faint acid and basic properties, and forms a crystalline *silver* salt, $\text{C}_8\text{H}_7\text{ON}_4\text{Ag}$, and a *hydrochloride*, $\text{C}_8\text{H}_8\text{ON}_4\text{HCl} + \text{H}_2\text{O}$, separating in white, acicular crystals.

Guanazole may be regarded as a symmetrical secondary hydrazine and as such it is capable of condensing with dicyanodiamide, forming a compound, guanazoguanazole, containing two guanazole rings in the molecule. The replacement of one or more of the four imino-groups in guanazoguanazole by oxygen atoms leads to the production of other condensed molecules; such of these compounds as have been prepared are described below.

Guanazoguanazole, $\text{NH} \begin{smallmatrix} \text{C(NH)} \cdot \text{N} \cdot \text{C(NH)} \\ \text{C(NH)} \cdot \text{N} \cdot \text{C(NH)} \end{smallmatrix} \text{NH}$, obtained by the action of guanazole hydrochloride on dicyanodiamide, or, better, by the interaction of 2 mols. of dicyanodiamide and 1 mol. of a hydrazine salt, crystallises from alcohol in small, shining plates, which, when heated on platinum, do not melt but gradually disappear without carbonising; when heated in a glass tube, it sublimes in the form of small, acicular crystals; it is slightly soluble in water and shows distinct basic functions. The hydrochloride is unstable; the *platinichloride*, with $2\text{H}_2\text{O}$, forms small, orange prisms; the *picrate*, $\text{C}_4\text{H}_6\text{N}_8\text{C}_6\text{H}_2\text{O}_7\text{N}_3$, separates from water in spheroidal aggregates of crystals which melt and decompose at above 270° and are slightly soluble in alcohol; with silver nitrate, it forms a *double* compound, $\text{C}_4\text{H}_6\text{N}_8\text{AgNO}_3$, obtained as a white precipitate. The *diacetyl* derivative, $\text{C}_4\text{H}_4\text{N}_8\text{Ac}_2$, and the *triacetyl* derivative, $\text{C}_4\text{H}_3\text{N}_8\text{Ac}_3$, obtained as a white powder, are insoluble in water and melt and decompose at a high temperature.

Iminourazoguanazole, $\text{NH} \begin{smallmatrix} \text{C(NH)} \cdot \text{N} \cdot \text{NH} \\ \text{C(NH)} \cdot \text{N} \cdot \text{CO} \end{smallmatrix} \text{C} \cdot \text{NH}$, obtained by dissolving guanazoguanazole in water containing just the requisite quantity of hydrochloric acid, and boiling the solution in a reflux apparatus until a small portion completely dissolves in potassium hydroxide solution, forms a white, crystalline powder insoluble in water.

It shows faintly basic properties, yielding with concentrated hydrochloric acid spheroidal crystalline aggregates of a hydrochloride which is decomposed by water or even in the air; it gives no picrate or platinichloride. Its acid properties are more marked, as it dissolves readily in potassium hydroxide solution, from which it is precipitated by acids.

Urazoguanazole, $\text{NH} \begin{array}{c} \text{C}(\text{NH}) \cdot \text{N} \cdot \text{CO} \\ \text{C}(\text{NH}) \cdot \text{N} \cdot \text{CO} \end{array} \text{NH}$, prepared by the interaction of molecular proportions of urazole and dicyanodiamide, or of guanazole and biuret, forms a white powder which is insoluble in water or alcohol and when heated in a small tube sublimes and partially decomposes with evolution of ammonia. In this compound, the basic properties have entirely disappeared, but the acid properties have become more marked.

Iminourazoiminourazole, $\text{NH} \begin{array}{c} \text{C}(\text{NH}) \cdot \text{N} \text{---} \text{CO} \\ \text{CO} \text{---} \text{N} \cdot \text{C}(\text{NH}) \end{array} \text{NH}$, obtained by the action of excess of dicyanodiamidine hydrochloride on hydrazine hydrochloride, separates from aqueous acetic acid as a white, indistinctly crystalline, infusible powder, which when heated on platinum does not melt but slowly disappears with formation of fumes.

α -*Naphthylguanazole*, $\text{C}_{10}\text{H}_7 \cdot \text{N} \begin{array}{c} \text{C}(\text{NH}) \cdot \text{NH} \\ \text{NH} \text{---} \text{C} \cdot \text{NH} \end{array}$, prepared from molecular proportions of dicyanodiamide and α -naphthylhydrazine hydrochloride, is deposited from aqueous solution in white, acicular crystals melting at 230° ; it has well-defined basic properties, forming well crystallised salts with acids. Its *hydrochloride* crystallises from alcohol in white prisms, which melt at 273° and dissolve readily in water. It gives a flocculent, yellow platinichloride and a well crystallised picrate.

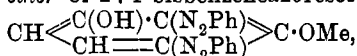
The authors propose a new method of nomenclature for guanazole and similar compounds, taking 1:2:4-triazole, $\text{NH} \begin{array}{c} \text{CH} \cdot \text{N} \\ \text{N} = \text{CH} \end{array}$, as the fundamental nucleus. The names of the compounds described in this paper would then become: guanazole, 3:5-di-iminotriazolidine; phenylguanazole and the other mono-substituted guanazoles, 1-phenyl-3:5-di-iminotriazolidine; phenylmethylguanazole, 1-phenyl-2 methyl-3:5-di-iminotriazolidine; iminourazole, 3:5-iminotriazolidone; phenyliminourazole, 1-phenyl-3-imino-5-triazolidone; guanazoguanazole, 3:5-di-iminotriazolidinyl-3:5-di-iminotriazolidine; iminourazoguanazole, 3:5-iminotriazolidone; urazoguanazole, 3:5-triazolidonyl-3:5-diiminotriazolidine; iminourazoiminourazole, 3:5-iminotriazolidonyl-3:5-iminotriazolidone.

T. H. P.

Two Modifications of Benzene-4-azoresorcinol and the Constitution of the Hydroxyazo-compounds. By WILLIAM R. ORNDORFF and E. D. THEBAUD (*Amer. Chem. J.*, 1901, **26**, 159—166. Compare Will and Pukall, *Abstr.*, 1887, 660, and Goldschmidt and Pollak, *Abstr.*, 1892, 974).—Diacetylbenzene-4-azoresorcinol, which is formulated by Goldschmidt and Pollak as $\text{OAc} \cdot \text{C} \begin{array}{c} \text{CH} \cdot \text{CH} \\ \text{CH} \text{---} \text{CO} \end{array} \text{C} \cdot \text{N} \cdot \text{N} \cdot \text{AcPh}$,

reacts with phenylhydrazine to form a *phenylhydrazone* which crystallises from benzene in deep-red granules and melts at 163° ; when hydrolysed, it gives the *bisphenylhydrazone* of 4-hydroxy-1:2-benzoquinone, $\text{OH}\cdot\text{C}=\text{CH}\cdot\text{C}:\text{N}\cdot\text{NHPh}$, which crystallises from dilute acetic acid in dark red needles and melts sharply at 160° .

The *monomethyl ether* of 2:4-bisbenzeneazoresorcinol,



prepared by the action of diazobenzene chloride on resorcinol monomethyl ether, crystallises from a mixture of chloroform and alcohol in short, red needles and melts at $189-190^{\circ}$.

Benzeneazoresorcinol monomethyl ether was found to melt at 123° ; Will (Abstr., 1888, 457) gives 114° as the melting point. T. M. L.

Sulphonated Hydroxyazo-colouring Matters and their Salts.

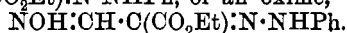
By PAUL SISLEY (*Bull. Soc. Chim.*, 1901, [iii], 25, 862—877).—Orange-II, $\text{SO}_3\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, is a very stable substance, the sodium being eliminated only by boiling with a large excess of concentrated hydrochloric acid. The product thus obtained crystallises in reddish-brown needles and is a powerful acid, readily decomposing sodium chloride or sulphate with the precipitation of Orange-II. Chrysoin, $\text{SO}_3\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, is more easily decomposed than Orange-II; the free acid forms small, steel-grey crystals and also has the power of decomposing metallic salts. Crystal-Ponceau, or Ponceau-6R, $\text{C}_{10}\text{H}_7\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_4(\text{SO}_3\text{Na})_2\cdot\text{OH}$, is only decomposed by heating with concentrated sulphuric acid; the free acid thus obtained forms small, red crystals and decomposes sodium hydrogen sulphate or phosphate in the cold. The powerful acid properties of these colouring matters afford a means of preparing a number of metallic salts, which are described in detail in the paper. N. L.

Action of Sodium and of Hydroxylamine on Ethyl Cyanoacetate Phenylhydrazone and the Sythesis of Ethyl Cyano-oxalacetate. By CORRADO BERTINI (*Gazzetta*, 1901, 31, i, 578—588).—The γ -phenylhydrazone of ethyl cyanoacetate (Weissbach, Abstr., 1898, i, 366), on treatment with aqueous alcoholic sodium hydroxide and subsequent precipitation with hydrochloride acid, behaves similarly to the β -compound (Krückeberg, Abstr., 1894, i, 369) in being transformed into the corresponding α -phenylhydrazine. In studying the further hydrolysing action of an alcoholic solution of sodium on these compounds, the author has hence confined himself to the α -derivative. When this compound is heated on the water-bath for an hour with an alcoholic solution of a molecular proportion of sodium, the addition of hydrochloric acid precipitates two substances:

(1) *Cyanoacetic acid phenylhydrazone*, $\text{CO}_2\text{H}\cdot\text{C}(\text{CN})\cdot\text{N}\cdot\text{NHPh}$, crystallising from water in shining, yellow plates which melt at 157° and on further heating decompose with evolution of carbon dioxide. It is very soluble in alcohol, acetone, or acetic acid, and slightly so in benzene. A purer product is obtained, although in smaller yield, by using Weissbach's γ -phenylhydrazone in place of the α -compound.

(2) *Cyanoformaldehyde phenylhydrazone*, $\text{CN}\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, which is obtained as sole product if a large excess of sodium is used in the reaction and the heating continued for a long time. It crystallises from water in long, slender, yellow needles melting at 162° and dissolves readily in alcohol, less so in boiling water, acetic acid, sodium hydroxide solution, or ammonium hydroxide, forming with the last-named a salt easily decomposed by heat. It forms silver, barium, copper, &c., salts. Its *nitroso*-compound, $\text{C}_8\text{H}_6\text{ON}_4$, crystallises from water in sparkling, yellow needles melting at $157\text{--}158^\circ$, and is soluble in alcohol or benzene and in alkali solutions, from which it is reprecipitated by acids; by double decomposition, copper, silver, barium, lead, &c., salts can be obtained. When hydrolysed with alcoholic potassium hydroxide, the phenylhydrazone yields large quantities of ammonia and a small proportion of a yellow substance which melts at 140° , and is probably the phenylhydrazone of glyoxylic acid already obtained by Elbers (*Abstr.*, 1885, 535). With diazobenzene acetate, an aqueous solution of the sodium salt of cyanoformaldehyde phenylhydrazone forms azophenylformazylmethane (formazylazobenzene), $\text{NHPh}\cdot\text{N}:\text{C}(\text{N}:\text{NPh})_2$.

The action of hydroxylamine on the α - or β -phenylhydrazones of ethyl cyanoacetate gives rise to two compounds: (1) A small quantity of a substance separating from water in yellowish-brown crystals melting at 162° ; it has the composition $\text{C}_{11}\text{H}_{15}\text{O}_3\text{N}_3$ and is either an amide, $\text{CONH}_2\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{NHPh}$, or an oxime,



(2) *Aminoisooxyazalone phenylhydrazone*, $\text{O} \begin{array}{c} \text{N}=\text{C}\cdot\text{NH}_2 \\ \diagup \\ \text{CO}\cdot\text{C}:\text{N}\cdot\text{NHPh} \end{array}$, which is precipitated from its solution in ammonia by dilute acids in the form of a canary-yellow, voluminous precipitate; this deflagrates at 165° without melting and hence cannot be analysed; it gives barium, silver, copper, lead, &c., salts and a crystalline sodium salt very soluble in water; its *acetyl* derivative crystallises from a mixture of ethyl and amyl alcohols in shining, yellow plates which redden at $178\text{--}180^\circ$, and decompose with evolution of gas at 182° .

Ethyl cyano-oxalacetate, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, is formed as sodium derivative when a mixture of ethyl oxalate and cyanoacetate in molecular proportion is gradually added to an absolute alcoholic solution of the corresponding quantity of sodium; it crystallises from ether or from a mixture of benzene and light petroleum in bundles of long, shining, silky-white needles melting at 98° and dissolves in alkali hydroxide solutions, from which it is precipitated by the addition of a mineral acid. Its alcoholic, but not its aqueous, solution is coloured an intense red by ferric chloride. When heated in ethereal solution with excess of phenylhydrazine, it yields the mono-phenylhydrazide of ethyl oxalate, $\text{NHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$. T. H. P.

Phenylhydrazine Phenylcarbazinate. By PAUL FREUNDLER (*Bull. Soc. Chim.*, 1901, [iii], 25, 859—862).—Phenylhydrazine phenylcarbazinate (see Fischer, *Abstr.*, 1878, 307) is obtained in theoretical quantity by passing a current of carbon dioxide into a cold solution of phenylhydrazine in ether or benzene. When exposed to

the air at the ordinary temperature it loses carbon dioxide and is converted into *phenylhydrazine hydrate*, $2\text{N}_2\text{H}_3\text{Ph}\cdot\text{H}_2\text{O}$, which melts at $23-24^\circ$. Phenylhydrazine phenylcarbazinate melts and decomposes at about 80° , and is insoluble in ether or benzene but slightly soluble in water. Attempts to effect its dehydration, with the production of diphenylcarbazide, were unsuccessful. The properties of the phenylcarbazinate render it useful in the recovery of phenylhydrazine from solutions and in separating it from other bases, such as aniline, *o*-toluidine, and *p*-bromophenylhydrazine, which do not form analogous compounds. N. L.

Hydrazo-compounds. II. Action of Hydrazobenzenes on Aldehydes. By BERTHOLD RASSOW (*J. pr. Chem.*, 1901, [ii], 64, 129—135. Compare following abstract).—Formaldehyde reacts readily with hydrazobenzene, producing, according to the conditions, either 1 : 2 : 4 : 5-tetraphenylhexahydro-1 : 2 : 4 : 5-tetrazine (m. p. 199° ; compare Bischoff, *Abstr.*, 1899, i, 279) or methylenebishydrazobenzene. Acetaldehyde and hydrazobenzene yield 3-methyl-1 : 2-diphenylhydrazimethylene and other similar compounds (*loc. cit.*). Other aldehydes with a normal carbon chain behave in an analogous manner, but heptaldehyde gives only a hexahydrotetrazine derivative.

p-Dinitrohydrazobenzene and 2 : 4 : 6-hexanitrohydrazobenzene do not react with formaldehyde. On the other hand, *s*-phenyl-*p*-tolylhydrazine and the three hydrazotoluenes very readily yield hexahydrotetrazine and methylenebishydrazo-derivatives. With acetaldehyde, these hydrazo-compounds do not give hydrazimethylene derivatives, but dimethyl-tetratolylhexahydrotetrazines.

Dibenzylhydrazine reacts with still greater ease with aldehydes.

K. J. P. O.

Action of Benzaldehyde and Aliphatic Aldehydes on Hydrazobenzene. By BERTHOLD RASSOW and MAX LUMMERZHEIM (*J. pr. Chem.*, 1901, ii, 64, 136—165. Compare preceding abstract).—*Methylenebishydrazobenzene*, $\text{CH}_2(\text{NPh}\cdot\text{NHPH})_2$, is obtained by mixing hydrazobenzene (2 mols.), dissolved in alcohol, with an aqueous solution of formaldehyde (1 mol.), and crystallises in plates melting at $145-146^\circ$. On warming the last-mentioned compound in alcoholic solution either alone or with formaldehyde, 1 : 2 : 4 : 5-tetraphenylhexahydro-1 : 2 : 4 : 5-tetrazine (m. p. 199°) is produced; with nitric acid, the latter gives a tetranitroazobenzene (m. p. 218°); by sulphuric acid, it is dissolved, forming a deep blue solution, and converted into benzidine.

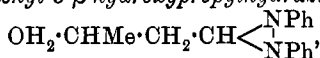
1 : 2-Diphenyl-3-methylhydrazimethylene, $\text{CHMe}\cdot\text{NPh}\cdot\text{NPh}$, prepared by

the interaction of molecular quantities of acetaldehyde and hydrazobenzene, forms white crystals melting at $150-151^\circ$. By the action of excess of acetaldehyde (3 mols.) on hydrazobenzene (1 mol.) in the presence of alcohol, 1 : 2-diphenyl-3- β -ethoxypropylhydrazimethylene,

$\text{OEt}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NPh}\cdot\text{NPh}$, is formed; it crystallises in rhombic

crystals melting at $67-68^\circ$, and is decomposed by dilute acids. When excess of acetaldehyde and hydrazobenzene react in the presence of

petroleum, 1 : 2-diphenyl-3-β-hydroxypropylhydrazimethylene,



is obtained as crystals melting at 116—117°. In the presence of methyl alcohol, 1 : 2-diphenyl-3-β-methoxypropylhydrazimethylene is produced and crystallises in white needles melting at 81—82°; this methoxy-compound can also be prepared by heating the ethoxy-derivative with methyl alcohol at 120°.

The condensation product obtained by Cornelius and Homolka (Abstr., 1886, 1026) from benzaldehyde and hydrazobenzene, and thought by them to be triphenylhydrazimethylene (hydrazoin) is shown by the authors to be a mixture of azobenzene and benzaldehyde. K. J. P. O.

Addition of Aldehydoaminic Bases to Naphthols. II. By MARIO BETTI [with CESARE SPERONI] (*Gazzetta*, 1901, 31, ii, 191—200. Compare this vol., i, 81, 753).—The authors discuss the reactions taking place between benzaldehyde and benzylideneanil-β-naphthol and between β-naphthol, benzaldehyde, and aniline, which both yield the same product, namely, 1 : 2 : 3-triphenyl-4 : 2-β-naphthoisoosoxazine (this vol., i, 611); with α-naphthol, the corresponding α-naphthoisoosoxazine is obtained. The action of acetic acid on the benzylideneanilnaphthols yields the corresponding 1 : 2 : 3-triphenyl-4 : 2-naphthoisoosoxazines.

Benzylidenephénylhydrazine-β-naphthol, $\text{NHPh} \cdot \text{NH} \cdot \text{CHPh} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, obtained by the action of phenylhydrazine on benzylideneanil-β-naphthol, crystallises from alcohol in small, white needles melting at 161°; it is readily decomposed by the action of cold dilute mineral acids, and with cold ferric chloride its benzene solution gives an intense violet coloration which disappears on adding excess of the ferric salt.

Benzylidenephénylhydrazine-α-naphthol crystallises from alcohol in white needles melting at 156°; with ferric chloride, it gives in the cold a transitory red coloration. T. H. P.

Action of Hypochlorous Acid on Diazobenzenesulphonic Acid. By THEODOR ZINCKE (*Ber.*, 1901, 34, 2853—2856).—Further researches to elucidate the constitution of the acid obtained (Abstr., 1896, i, 169) by the oxidation of *p*-diazobenzenesulphonic acid with hypochlorous acid. The oxidation of 6-diazo-*m*-xylene-4-sulphonic acid is shown to yield the corresponding azo-*m*-xylenedisulphonic acid, and therefore the acid described in the previous paper is 2 : 2'-dinitroazobenzene-4 : 4'-sulphonic acid, its formation being always accompanied by that of 4 : 6-dichloro-*o*-nitroaniline. This acid, when treated with hydrochloric acid, yields 2 : 2' : 4 : 4'-tetrachloroazobenzene, which crystallises in small, slender needles melting at 161—162°, and when treated with hydrogen bromide gives 1 : 2 : 3 : 5-tetrabromobenzene. R. H. P.

Action of Diazobenzene on some Aliphatic Aldehydes and Ketones. By EUGEN BAMBERGER and JENS MÜLLER (*J. pr. Chem.*, [ii], 64, 199—221).—A more detailed account of work already published (compare Abstr., 1893, i, 127, 182, 183).

Formazyl Methyl Ketone. By EUGEN BAMBERGER and PAUL DE GRUYTER (*J. pr. Chem.*, [ii], 64, 222—244).—A more detailed account

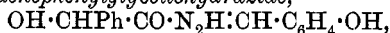
of work already published (compare Abstr., 1893, i, 157; 1894, i, 23, 98).

Formation of Ethyl Allophanate from the Azoimides of Hydroxy-acids. By THEODOR CURTIUS and C. MULLER (*Ber.*, 1901, 34, 2794—2799).—On diazotising the hydrazide of mandelic acid, an oily azoimide is obtained, which is highly unstable, and immediately undergoes hydrolysis: $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{N}_3 + \text{H}_2\text{O} = \text{Ph}\cdot\text{CHO} + \text{N}_2 + \text{NH}_3 + \text{CO}_2$. When the diazotisation is incomplete, the benzaldehyde, formed by hydrolysis, condenses with unchanged hydrazide, producing benzylidenephénylglycolohydrazide, $\text{CHPh}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CHPh}$. With aniline, the azoimide reacts, forming mandelic anilide. On evaporation of a solution of the azoimide in alcohol-ether, phenylglycolourethane and ethyl allophanate are formed; the latter is either the result of the interaction of the urethane and azoimide: $\text{OH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et} + \text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{N}_3 = 2\text{Ph}\cdot\text{CHO} + \text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et} + \text{N}_2$, or of 2 mols. of the urethane: $2\text{OH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et} = \text{EtOH} + 2\text{Ph}\cdot\text{CHO} + \text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$.

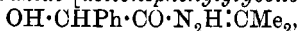
Only the azoimides of hydroxy-acids containing the secondary alcohol group, $\text{CH}\cdot\text{OH}$, yield ethyl allophanate with alcohol; thus glycolazide yields only glycolurethane, which is hydrolysed by strong acids to formaldehyde, ammonia, carbon dioxide and alcohol, whilst lactazide readily gives ethyl allophanate; from β -hydroxypropionazide, on the other hand, only a urethane is formed.

Phénylglycolohydrazide, $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{N}_2\text{H}_5$, prepared from ethyl mandelate and hydrazine hydrate, crystallises in leaflets melting at 132° and dissolves in sulphuric acid with a transient blood-red colour; the *hydrochloride* is a crystalline powder melting at $149\text{--}150^\circ$; the *sodium salt* a yellowish-brown powder melting and decomposing between 215° and 220° .

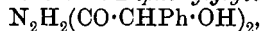
Benzylidenephénylglycolohydrazide, formed when the components are mixed in aqueous solution, crystallises in needles melting at 149° . *o-Hydroxybenzylidenephénylglycolohydrazide*,



forms needles melting at 179° ; *cinnamylidenephénylglycolohydrazide*, $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{N}_2\text{H}:\text{CH}\cdot\text{CH}:\text{CHPh}$, needles melting at 180° ; *propylidenephénylglycolohydrazide* [*acetonephénylglycolohydrazide*],



leaflets melting at $134\text{--}135^\circ$. *s-Diphenylglycolohydrazide*,



is prepared by the action of iodine on phenylglycinohydrazide dissolved in alcohol, and crystallises in silky needles melting at 225° .

K. J. P. O.

Precipitation of Proteids by Anhydrous Sodium Sulphate. By S. N. PINKUS (*J. Physiol.*, 1901, 27, 57—65).—Anhydrous sodium sulphate possesses at 30° the same precipitating power of proteids as ammonium sulphate. It precipitates globulins at the point of half saturation (25 per cent.), and albumins at full saturation: it also allows of fractionation of proteoses. The proteid colour reactions are hardly at all interfered with; the nitrogen of the precipitate can be estimated directly: it is easy to obtain solutions containing only 5

per cent. of salt, and the salt itself is practically non-toxic. By adding to proteid solutions enough of the salt to absorb all the water, a product is obtained which can be preserved without change in the proteid. These are some of the advantages of the method. W. D. H.

Decomposition of Albumin. By MAXIMILIANO DENNSTEDT (*Chem. Zeit.*, 1901, 25, 814—815).—In opposition to Kossel (this vol., i, 107), the author insists on the absolute necessity for the analysis of every form of proteid and also of all intermediate decomposition products. The drying of proteid substances should be accomplished in a desiccator over phosphoric oxide or in an oven at 100°, not at 110—120°, since combined water is driven off at this temperature. J. J. S.

Formation of Carbamide by the Oxidation of Albumin. By FRIEDRICH N. SCHULZ (*Zeit. physiol. Chem.*, 1901, 33, 363—369 Compare Jolles, this vol., i, 490).—Jolles' method is criticised, especially from the point of view that it is impossible to remove all the salt by precipitation with alcohol, even when the operation is repeated 7 to 8 times. It is found that the carbamide oxalate obtained after such treatment may yield as much as 10 per cent. of ash. J. J. S.

Formation of an Isatin Derivative from Albumin. By JULIUS GNEZDA (*Compt. rend.*, 1901, 133, 517—518).—When peptone is boiled with hypochlorous acid solution, it yields a very small quantity of a substance which seems to be identical with chloroisatin and has none of the properties of indole derivatives (compare Abstr., 1899, ii, 715). C. H. B.

A Chlorinated Casein and its Decomposition Products with Fuming Hydrochloric Acid. By THEODOR PANZER (*Zeit. physiol. Chem.*, 1901, 33, 131—150. Compare Habermann and Ehrenfeld, this vol., i, 622).—A chlorocasein obtained by the action of nascent chlorine (from hydrochloric acid and potassium chlorate) on casein has the following percentage composition: C, 47.05; H, 5.52; N, 12.40; S, 0.32; Cl, 8.32; P, 0.81; O, 25.67. It dissolves in dilute alkalis, but the solutions obtained have an acid reaction and are also capable of liberating carbon dioxide from carbonates. Salts of heavy metals yield precipitates, but the ordinary reagents for alkaloids, with the exception of potassium bismuth iodide, do not give precipitates with the substance.

For the preparation of the potassium derivative, 459 parts by weight of chlorocasein are required for every equivalent of the metal, for the silver derivative, 234.2 and for the copper, 463.4 parts by weight.

Among the products of the action of concentrated hydrochloric acid on this chlorocasein are chlorinated acids free from nitrogen, chlorinated nitrogenous humic acid, glutamic acid, leucine, and phosphoric acid. The presence of the following substances has been established: aspartic acid, arginine, histidine, and lysine, but not tyrosine. It is probable that the chlorine replaces amino-groups, hydrogen atoms, and possibly certain hydroxyl groups in the casein molecule. J. J. S.

Hydrolysis of Casein by means of Hydrochloric Acid. By EMIL FISCHER (*Zeit. physiol. Chem.*, 1901, 33, 151—176. Compare Cohn, Abstr., 1896, i, 658; 1898, i, 343; 1899, i, 315; 1900, i, 466).—The method previously described (this vol., i, 192) has been employed

for the separation of the amino-acids formed by the hydrolysis of casein with hydrochloric acid. In addition to the products obtained by others, the presence of the following amino-acids has been established—aminovaleric acid, phenylalanine, pyrrolidine-2-carboxylic acid, and probably glycine. These amino-acids are partially racemised by the esterification process and to isolate them it is advisable to completely racemise them by heating with baryta water under pressure and then to combine them with phenylcarbimide.

Aminovaleric acid phenylcarbimide crystallises from 50 per cent. alcohol in hexagonal plates melting and decomposing at 157—158° and yields an *anhydride*, $C_{12}H_{14}O_2N_2$, melting at 117°. *l-Pyrrolidine-2-carboxylic acid* is also present in addition to the racemic acid. It melts and decomposes at 203—206°, and at 20° has $[\alpha]_D - 77.40^\circ$ in aqueous solution, $[\alpha]_D - 46.53$ in 20 per cent. hydrochloric acid solution and $[\alpha]_D - 83.48$ in potassium hydroxide solution; its *phenylcarbimide* derivative, which was only obtained in the form of a resin, yields an *anhydride*, $C_{12}H_{12}O_2N_2$, crystallising in small prisms or flat needles melting at 144° (corr.). The copper salts of some of these amino-acids vary in solubility with the presence or absence of other amino-acids; for example, copper aminovalerate becomes soluble in absolute alcohol when *l*-pyrrolidine-2-carboxylic acid is present, and copper leucine and copper aminovalerate crystallise together in large prisms readily soluble in water and apparently form a molecular compound. The ester from phenylalanine is readily separated from the esters of glutamic and aspartic acids, which have approximately the same boiling points, by treatment with water. J. J. S.

A Hydrolytic Product from Edestin, its Relationship to Weyl's Albuminate and to the Histone Group. By THOMAS B. OSBORNE (*Zeit. physiol. Chem.*, 1901, 33, 225—239. Compare Weyl, *ibid.*, 1877, 1, 72).—Water and dilute acids transform edestin into a substance—*edestan*—insoluble in sodium chloride solutions of medium strength and identical with Weyl's albuminate. It is a true hydrolytic product and is probably the first substance formed in the hydrolysis of edestin to acid albumin. The percentage composition is practically the same as that of edestin; it forms salts with hydrochloric acid which are strongly acid to phenolphthalein. Edestan is insoluble in water or dilute ammonia and less soluble than edestin in potassium hydroxide solution. It gives most of the reactions which are characteristic of histones (Bang, *Abstr.*, 1899, i, 836) although it appears to have little in common with true histones. J. J. S.

The Basic Nature of the Proteid Molecule and the Behaviour of Edestin to Known Quantities of Acid and Alkali. By THOMAS B. OSBORNE (*Zeit. physiol. Chem.*, 1901, 33, 240—292).—The proteids are basic substances and form true salts with acids. The usual proteid preparations, which are either neutral or acidic to litmus, are really proteid salts. The free bases are best obtained by adding sodium or potassium hydroxide until the product is neutral to phenolphthalein. Preparations of edestin consist essentially of chloride when crystallised from sodium chloride, and of sulphate when crystallised from ammonium

sulphate; when crystallised from a mixed medium, the salt formed is that with the negative ion which is present in largest quantity.

Water separates ordinary edestin chloride into a soluble part, *edestin dichloride*, and an insoluble part, the *monochloride*, both salts being isomorphous with edestin itself. To completely dissolve edestin, slightly more than the theoretical amount of hydrochloric acid, calculated on the assumption that 1 mol. of the base (mol. wt. 14500) combines with 2 mols. of the acid, is required, since a certain amount of hydrolytic dissociation occurs. The sulphates are less soluble than the chlorides and so far have not been obtained pure. Phosphoric acid behaves as a monobasic acid towards edestin and for the complete solution of edestin in either this acid or in acetic acid only slightly more than the theoretical amount of acid is required. *Edestin dinitrate* is much more soluble in pure water at 30° than at 20°.

Edestin also dissolves in alkalis; with sodium or potassium hydroxide, complete solution occurs when alkali and proteid are present in mol. proportion; with ammonia or sodium carbonate, however, a considerable excess of the alkali is required. The solutions in sodium or potassium hydroxide become cloudy when kept, probably owing to hydrolysis. The solubilities of edestin in water and in neutral sodium chloride solution are those of a globulin. Edestin monochloride, although insoluble in water, dissolves in saline solutions; the dichloride and sodium and potassium edestin are soluble in water or concentrated saline solutions, but insoluble in very dilute saline solutions. J. J. S.

Behaviour of Oxyhæmoglobin, Carbon Monoxide Hæmoglobin, Methæmoglobin, and certain of their Derivatives in the Magnetic Field, with a Preliminary Note on the Electrolysis of the Hæmoglobin Compounds. By ARTHUR GAMGEE (*Proc. Roy. Soc.*, 1901, 68, 503—512).—Oxyhæmoglobin, carbon monoxide hæmoglobin, and methæmoglobin are found to be decidedly diamagnetic, whilst the iron-containing derivatives, hæmatin and acethæmin, are very strongly magnetic. The electrolysis of solutions of oxyhæmoglobin and carbon monoxide hæmoglobin shows that very probably the iron-containing group is (or is part of) an electronegative radicle; the iron in such a group generally exhibits diamagnetic properties. J. C. P.

Arnold's Neutral Hæmatin. By K. H. L. VAN KLAVEREN (*Zeit. physiol. Chem.*, 1901, 33, 293—309. Compare Arnold, *Abstr.*, 1900, i, 318; Formánek, *ibid.*, 532).—Arnold's neutral hæmatin is a proteid, differing in composition only slightly from hæmoglobin, the main difference being a lower percentage of iron. It is not a true hæmatin and for it the author suggests the name kathæmoglobin; the pure compound is best obtained by treating a concentrated solution of hæmoglobin crystals with 96 per cent. alcohol and saturated potassium hydroxide solution, warming to 60°, immediately neutralising, filtering, and pouring into distilled water; it may be purified by solution in 60 per cent. alcoholic sodium chloride solution and precipitation with water. On treatment with very dilute hydrochloric acid, kathæmoglobin, like oxyhæmoglobin, is converted into a hæmatin and a globin. The hæmatin from kathæmoglobin contains less iron than that from oxyhæmoglobin; and

thus the name hæmatin comprises a group of compounds which differ from one another, but which probably contain a nucleus in common.

J. J. S.

Hæmocyanin. By MARTIN HENZE (*Zeit. physiol. Chem.*, 1901, **33**, 370—384).—Hæmocyanin was separated in a crystalline form from the blood of the octopus by the method introduced by Hopkins and Pinkus for crystallising proteids. It is not precipitated from its solutions by dialysis, nor can it readily be "salted out"; it is, therefore, not a globulin, as Halliburton considered. It is coagulated by heat at 68—72°. Its elementary composition is C, 53·66; H, 7·33; N, 16·09; S, 0·86; Cu, 0·38; O, 21·67 per cent. It gives the biuret (red-violet) reaction without the addition of copper sulphate. It is regarded as a copper albuminate, in which the copper is loosely combined, and can be readily split off by hydrochloric acid. One hundred c.c. of octopus blood yield 3·4 c.c. of oxygen, and 9 per cent. of hæmocyanin. One gram of hæmocyanin, therefore, combines with 0·4 c.c. of oxygen; that is about one-fourth of that held by hæmoglobin.

W. D. H.

Fibroin from Silk. By EMIL FISCHER and ALADAR SKITA (*Zeit. physiol. Chem.*, 1901, **33**, 177—192. Compare Weyl, *Abstr.*, 1888, 857; Wetzel, *ibid.*, 1899, i, 466).—Among the products obtained from silk fibroin by hydrolysis with hydrochloric acid are *l*-tyrosine, 10 per cent.; *d*-alanine, 21 (*Abstr.*, 1899, ii, 888); *l*-phenylalanine, 1—1·5; *l*-leucine, 1—1·5; glycine, 36, and other amino-acids. The method adopted for the separation of the acids was that previously described (this vol., i, 192). The *d*-alanine corresponds in configuration with *d*-lactic acid.

J. J. S.

Decomposition Products of Proteids. By EDWIN HART (*Zeit. physiol. Chem.*, 1901, **33**, 347—362. Compare Kossel and Kutscher this vol., i, 107).—The heteroalbumose and protoalbumose, obtained when santonin is digested with pepsin, differ in the amounts of hexon bases they yield. The heteroalbumose contains less histidine, but is richer in arginine than the protoalbumose. The heteroalbumoses obtained by coagulation and by precipitation with alcohol are apparently identical.

The amounts of ammonia and lysine produced on the hydrolysis of casein or glue with boiling acids are greater when mineral salts, for example, sodium chloride or sulphate, are present during the hydrolysis. The humin formed by the acid hydrolysis of glue in the presence of sodium chloride is free from nitrogen, and that obtained from casein yields no lysine on hydrolysis with sulphuric acid in the presence of sodium chloride. Zein, even in the presence of sodium chloride, yields no lysine.

J. J. S.

A Crystalline [Peptone-Serum Product] ("Immunisierungsprodukt"). By HANS BUCHNER and L. GERET (*Chem. Centr.*, 1901, ii, 704; from *Münch. med. Woch.*, **48**, 1163—1164).—When the serum from rabbits which have been treated with peptone or with ox blood is added to a solution of pure peptone prepared by Kühne's method, a

precipitate is formed which consists of globulites or spherical masses of crystalline material arranged in concentric layers. The globulites are strongly refractive, and insoluble in hot nitric or hydrochloric acid, or in cold sulphuric acid, acetic acid, alcohol, or pepsin-hydrochloric acid, but dissolve in hot sulphuric acid; they give an intense coloration with iodine, but neither show Millon's nor the biuret reaction. When treated with ammonia, they swell to a slight extent, but much more with potassium hydroxide solution. On ignition, a residue of ash of precisely the same form is left; it probably consists of calcium compounds, for by the action of concentrated sulphuric acid on the globulites, calcium sulphate is formed. E. W. W.

A Ferment which Produces Mannitol. By ULYSSE GAYON and ELISÉE DUBOURG (*Ann. Inst. Pasteur*, 1901, 15, 527—569).—A full description of the fermenting power of the enzyme producing mannitol from lævulose, which has been described by the authors (*ibid.*, 1894, 8, 108). The enzyme ferments hexoses, pentoses, and saccharoses (without previous hydrolysis), forming carbon dioxide, acetic, lactic, and succinic acids and glycerol; mannitol is formed only in the case of lævulose, ethyl alcohol being obtained from other sugars. It is noteworthy that the sugars not fermented by yeast are decomposed by the mannitol ferment. The enzyme thus affords a means of detecting lævulose in mixtures of fermentable carbohydrates. R. H. P.

Oxydase and Peroxydase Reactions. By F. W. T. HUNGER (*Chem. Centr.*, 1901, ii, 648; from *Ber. deutsch. Bot. Ges.*, 19, 374—377).—The detection of oxidising enzymes by the guaiacum-hydrogen peroxide reaction is frequently interfered with not only by tannins but also by other substances. The milk from young cocoanuts, for instance, contains a sugar (not sucrose) which completely inhibits the reaction, but the milk from older fruit gives the coloration, although rather indistinctly. A solution of the enzyme obtained by treating the milk with 95 per cent. alcohol and redissolving the precipitate shows the reaction very distinctly, but when dextrose is previously added to the solution, the test fails. The milk from very old fruit which has not germinated and in which the sugar is completely changed to fat shows the reaction satisfactorily. The reducing effect has also been proved in the case of the sugar cane oxydases and other reducing agents such as hydrogen sulphide, hydrocyanic acid, pyrogallol, hæmatoxylin and brazilin also interfere with the reaction. Dilute acids destroy the coloration but it is re-formed on addition of alkali. According to Raciborski, the growing points of plants give the most intense coloration and these have been found by Went to be absolutely devoid of dextrose. E. W. W.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Refractive Index and Dispersion of Bromine. By CHARLES RIVIÈRE (*Compt. rend.*, 1900, 131, 671—672).—The author has determined the refractive index of bromine by means of the Fizeau-Foucault fringes for wave-lengths between 7909 and 5390, and at temperatures from 10° to 25°. The refractive index for the line *A* is 1.6394 at 10° and 1.6305 at 20°, and for the line *D*₂ 1.6543 at 20°. At 20° the dispersion between *A* and *D* is 0.037, which is greater even than that of carbon disulphide.
C. H. B.

Contributions to the Theory of Photographic Development. By J. PRECHT (*Chem. Centr.*, 1900, ii, 617; from *Arch. wiss. Phot.*, 2, 155—157).—The author considers that Luther's experimental results (*Abstr.*, 1900, ii, 253) are equally well explained by the assumption of the formation of the compound $\text{Ag}_2\text{O}, 2\text{AgCl}$, and do not prove the formation of a subchloride.
L. M. J.

Researches on the Silver Germ Action in Development. By J. PRECHT and WILHELM STRECKER (*Chem. Centr.*, 1900, ii, 617—618; from *Arch. wiss. Phot.*, 2, 158—164).—Against the views of Ostwald and Abegg (*Abstr.*, 1900, ii, 253) the authors urge the following objections. The impossibility of developing under-exposed images completely through the film; the slowness of the lateral broadening of the illuminated parts; the impossibility of increasing a thin veil to a reasonable density. These objections do not apply to the authors' theory that the silver bromide is altered, it may be but

physically, by the light so as to be rendered capable of reduction by the developer. A plate was covered by a thin emulsion and then one half coated by a similar emulsion; it was exposed and after exposure the single coating received a second emulsion. On development, it was found that the original double layer gave the denser image. The authors consider that this supports their views, as according to the silver germ theory the two halves should be of equal density.

L. M. J.

Electrode Potentials. By N. T. M. WILSMORE (*Zeit. physikal. Chem.*, 1900, 35, 291—332).—The expression $RT/n \cdot \log_e P$, where P is the electrolytic solution pressure, or more generally, an integration constant, is termed 'electrolytic potential,' and the relative values of this expression are given for 31 elements. The solutions in contact with the electrodes are supposed to be of normal ionic concentration, and the electrolytic potential of the hydrogen electrode is taken as zero. The results of earlier workers, as well as those of the author himself, are incorporated in the calculations. The hydrogen electrode has been fully investigated, and a form suitable as a normal electrode is described. On the basis of this new standard, the normal calomel electrode has the potential -0.283 volt. In the course of the experiments it was found that the E.M.F. of the hydrogen-oxygen gas cell slowly rises, and with normal sulphuric acid as electrolyte reaches the constant value 1.119 volt in 4—6 days.

The behaviour of air—and various metallic electrodes has been investigated from the point of view of their serviceableness as normal electrodes. With acid electrolytes, platinum points previously subjected to cathode polarisation, are found to be serviceable standard electrodes, inferior perhaps to mercury and lead, but preferable to zinc and cadmium electrodes immersed in solutions of their salts. With alkaline electrolytes, the only approximately satisfactory electrode is $\text{Hg} \mid \text{Hg}_2\text{O}$.

J. C. P.

Absolute Potentials of the Metals and Remarks on Normal Electrodes. By WILHELM OSTWALD (*Zeit. physikal. Chem.*, 1900, 35, 333—339).—The author criticises the introduction of the hydrogen electrode as a normal electrode (see Wilsmore, preceding abstract), and points out the advantages possessed by the older normal calomel electrode— $N/10 \text{ KCl}, \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$. A table is added giving Wilsmore's values in absolute potentials, the difference between the normal hydrogen and calomel electrodes being taken as 0.283 volt—the value given by that author.

J. C. P.

Chemical Actions Caused by the Silent Electric Discharge and the Conditions under which they take place. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 131, 772—781. Compare Abstr., 1878, 371).—A review of the chemical changes caused by the silent electric discharge and the effect of varying the potential between the two surfaces bounding the dielectric.

The potential of the atmosphere on a calm day, at an altitude of 28 m. is from 600—800 volts above that of the earth's surface, which is of course zero, and this difference of potential increases by about 20—30 volts for an increase in height of 1 m. This difference of

potential between different layers of air, or between the earth and the air above it, produces a silent electric discharge, the effects of which are in every way analogous to those produced in an ordinary ozoniser, and may account for the presence of ozone, oxides of nitrogen, ammonium nitrate, &c., in the atmosphere.

The formation of nitric acid when hydrogen, sulphur, &c., burn in air, and the changes which take place when a gas is heated to a high temperature and then allowed to come in contact with a cold surface, may be due to the silent electric discharge, the production of which is explained thus: electrification is developed in a gas which is at a high temperature, more especially if the temperature is not uniform throughout the whole mass of the gas. Now when a portion of such a gas is cooled by a cold surface, the layer of gas which is in direct contact with the cold surface is practically a dielectric, since it is necessarily at a low temperature, whereas the layers of gas above it, which are at a high temperature, possess a certain electrical conductivity. A silent electric discharge will therefore take place between the layers at a high temperature and the cold surface introduced, this discharge taking place through the cooled layer of gas directly in contact with the cold surface.

H. R. LE S.

Diffusion of Ions Produced in Air by the Action of a Radio-active Substance, Ultra-violet Light, and Point Discharges. By JOHN S. TOWNSEND (*Proc. Roy. Soc.*, 1900, 67, 122—124).—The diffusion coefficient was calculated from observations on the loss of conductivity of the gas as it passes along metal tubing. It was found that the negative ions produced when ultra-violet rays fall on zinc, diffuse into air at the same rate as the negative ions produced by a radio-active substance, the values of the coefficient being 0.0435 and 0.0375 cm.²/second in dry and moist air respectively at 17°. The ions produced by point discharges varied considerably, the negative ions have a diffusion coefficient in dry air varying from 0.037—0.032, that of the positive ions varying from 0.0247 to 0.0216; the values in moist air are slightly higher.

L. M. J.

Electro-striction of Ions in Organic Solvents. By GIACOMO CARRARA and M. G. LEVI (*Gazzetta*, 1900, 30, ii, 197—217).—The molecular volumes of several electrolytes and non-electrolytes in solution in organic solvents and in water have been measured for various concentrations, the results being calculated by the formula $\phi = A/Q - 1000 (S/Q - 1)/m$, where ϕ is the molecular volume of the solute in the solution, A its equivalent weight, Q the sp. gr. of the solvent (at 25°/4°), S the sp. gr. of the solution, and m the number of gram-molecules of solute in a litre of solution. The results agree in general, although there are exceptions, with the electro-striction theory of Drude and Nernst (*Zeit. physikal. Chem.*, 1894, 15, 79), the diminution of ϕ as the dilution increases being great or small according as the change in degree of dissociation is great or small. Also the smaller the dissociation in solution, the more nearly do the values of ϕ agree with those of the molecular volumes of the dissolved substances. The following table is for methyl alcoholic solutions, V being the dilution.

| | Molecular volume. | ϕ . | V . |
|--------------------|-------------------|----------|--------|
| Naphthalene..... | 111.79 | 116.88 | 4.097 |
| Carbamide | 45.18 | 37.76 | 0.945 |
| Cadmium iodide ... | 122.40 | 126.29 | 1.637 |
| „ | — | 121.67 | 13.096 |

The results for trichloroacetic acid in various solvents are as follows :

| | Molecular volume. | ϕ . | V . |
|---------------------|-------------------|----------|-------|
| Methyl alcohol..... | 101.11 | 96.69 | 3.252 |
| Ethyl alcohol | 101.11 | 92.59 | 1.94 |
| Acetone | 101.11 | 94.76 | 3.252 |
| Water | 101.11 | 85.44 | 3.77 |

T. H. P.

Electromotive Force and Osmotic Pressure. By R. A. LEHFELDT (*Zeit. physikal. Chem.*, 1900, 35, 257—282).—By means of a reversible cycle process, an expression is deduced for the E.M.F. of a concentration cell of the type :—metal | dilute salt solution | concentrated salt solution | metal. From the formula, which is applicable both to dilute and concentrated solutions, it follows that the E.M.F. of such a cell depends on the total osmotic pressure of the salt, and not on that of the metallic ions only. Experiments are described in which the E.M.F.s of concentration cells containing zinc chloride and sulphate have been determined. From the numbers thus obtained, and those given by other workers, the osmotic pressures in concentrated solutions of zinc chloride and sulphate have been calculated with the formula referred to. When P is the osmotic pressure, and V the volume which contains 1 gram equivalent, the expression PV/i should be constant in so far as the gaseous laws are exactly applicable. With increasing concentration, the value of PV/i for zinc chloride rises from the first, whilst in the case of zinc sulphate it first diminishes, reaches a minimum, and then steadily increases.

When the potential difference between metal and electrolyte is regarded as proportional to $\int PdV$, the electrolytic solution pressure of zinc must have the enormous value of 10^{19} atmospheres. The author points out that if the potential difference is made proportional to $\int VdP$, the electrolytic solution pressure of zinc has quite a moderate value—about 20,000 atmospheres (compare Abstr., 1900, ii, 62).

J. C. P.

Study of Hydrolytic Dissociation by means of Electrical Conductivity. By ROBERTO SALVADORI (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 177—180).—The electrical conductivities of dilute solutions of various salts, which in aqueous solution are hydrolytically dissociated, have been measured (1) alone and (2) in presence of added acid or base. In the latter case, hydrolytic dissociation is prevented, so that the electrical conductivity is that due only to electrolytic dissociation, which is diminished in degree by the addition of the acid or base. The salts examined were potassium carbonate in water and in $N/100$ potassium hydroxide solution and barium, copper, and lead

nitrates in water, and in $N/100$ nitric acid. In the case of the potassium carbonate, the difference between the two conductivities increases very considerably with the dilution, indicating a large increase in the hydrolysis. With copper nitrate, the differences found for the more concentrated solutions are the same as those for corresponding solutions of the non-hydrolysed barium nitrate, so that copper nitrate does not undergo appreciable hydrolysis in concentrated solution; only in very dilute solutions is the difference for barium nitrate less than that for copper nitrate, which hence only suffers slight hydrolysis in dilute solutions. For lead nitrate, the differences in conductivity show a decided increase as the dilution becomes greater, but even in the most dilute solutions the numbers are smaller than those for barium nitrate.

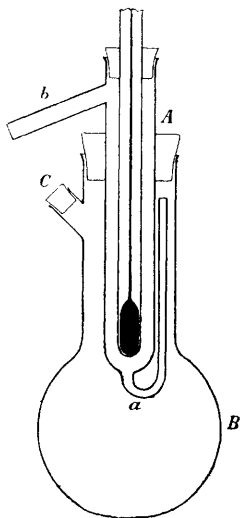
T. H. P.

Electrolytic Solution Pressure. By R. A. LEHFELDT (*Zeit. physikal. Chem.*, 1900, 35, 369).—A reply to Krüger's criticism (*Abstr.*, 1900, ii, 706).

J. C. P.

New Method for the Exact Determination of the Boiling Point. By A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 86—91).—The apparatus used in this modification of Landsberger's method (*Abstr.*, 1898, ii, 283) resembles that described by McCoy (*Abstr.*, 1900, ii, 387), but differs from it in that the vapour of the boiling solvent from the flask *B* passes through the tube *a* sealed in the bottom of the inner boiling tube *A*, which contains the solution. The variation in the thermometer reading due to variation in the rate of passage of the vapour is prevented by introducing a cylinder of platinum gauze into the boiling tube *A*. The author considers that, if the apparatus is carefully used, and the errors due to slight changes in the atmospheric pressure are eliminated by having for comparison a similar vessel filled with water, the results are more accurate than those obtained with Beckmann's apparatus.

J. C. P.



Magnetic Rotation of the Plane of Polarisation in Liquefied Gases under Atmospheric Pressure. I. By L. H. SIERTSEMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 70—74).—The author sketches and describes an apparatus used to determine magnetic rotation in liquefied gases. From preliminary experiments with methyl chloride, it is shown that the dispersion is about the same as for most gases. In the following table, w/w_D is the ratio of the rotation to that for sodium light.

| λ . | w/w_D (CH_3Cl). | w/w_D (gases). |
|-------------|-------------------------------------|------------------|
| 0.631 | 0.90 | 0.87 |
| 0.546 | 1.17 | 1.17 |
| 0.480 | 1.58 | 1.53 |
| 0.449 | 1.76 | 1.76 |
| 0.435 | 1.90 | 1.90 |

J. C. P.

Acetals of Monohydric Alcohols. By MARCEL DELÉPINE (*Compt. rend.*, 1900, 131, 684—686).—The following results were obtained,

| | Heat of combustion. 1 gram. | Molecular heat of combustion. | | Heat of formation. |
|-------------------|-----------------------------------|-------------------------------|---------------|-----------------------|
| | | Const. vol. | Const. press. | |
| Diethylformal ... | 7429·1 cal. | 772·62 Cal. | 773·75 Cal. | 111·75 Cal. |
| Dipropylformal.. | 8205·1 | 1083·07 | 1084·8 | 127·3 |
| Diisobutylformal | 8697·4 | 1391·57 | 1393·85 | 144·85 |
| Diisoamylformal. | 9064·5 | 1704·12 | 1707·0 | 158·3 |
| Dimethylacetal... | 6873·3 | 619·0 | 619·9 | 102·3 |
| Diethylacetal ... | 7872·2 | 928·9 | 930·35 | 118·45 |

The difference between two consecutive homologues is practically constant and is 155—156 Cal., although the deviations from this value are a little greater with the acetals than with the formals. The heat of formation of acetals and formals from alcohols and acetaldehyde and formaldehyde respectively is very small, but seems to increase with the molecular weight of the alcohols. C. H. B.

Thermochemical Researches on the Principal Opium Alkaloids. By ÉMILE LEROY (*Ann. Chim. Phys.*, 1900, [vii], 21, 87—144).—A detailed account of work already published (compare Abstr., 1899, ii, 465, 631; 1900, ii, 261). G. T. M.

Berthier's Method for Determining the Calorific Value of Fuels. By UBALDO ANTONY and E. DI NOLA (*Gazzetta*, 1900, 30, ii, 218—224).—Two common objections to Berthier's method of measuring the calorific value of fuels, in which the lead obtained on heating the fuel with litharge is weighed, are (1) that volatile products are evolved at temperatures lower than that at which reduction of the litharge takes place, and (2) that the heats of combustion of the different elements of the fuel are not proportional to the amounts of oxygen which they take up on burning. From a number of trials with different kinds of coal, the authors conclude that, if care is taken to heat the mixture of fuel and litharge slowly, reduction of the latter occurs without the evolution of any volatile matter. In the case of ordinary fuels, the error introduced into the calculation of calorific power by assuming that all the lead obtained is due to carbon, is very small and may be neglected. The available hydrogen in a fuel may be measured by heating it in a graphite crucible with lead fluoride, the reduction of which to metal is due entirely to the hydrogen. If p_C is quantity of lead obtained by the reduction of litharge, and p_H that formed from the fluoride, the calorific power of the fuel is given by the formula :

$$P = \frac{p_C}{34\cdot5} \times 8083 + \frac{p_H}{103\cdot5} \times 29367 \text{ (calories).}$$

T. H. P.

Vapour Pressure of Binary Liquid Mixtures. By JAN VON ZAWIDZKI (*Zeit. physikal. Chem.*, 1900, 35, 129—203).—The author has determined by means of apparatus described in the paper, the vapour pressure at certain temperatures in the case of a number of binary liquid mixtures, the composition being varied from 0 : 1 to 1 : 0.

The composition of the distillate being determined from its refractive index, the partial pressures in each mixture were calculated. The mixtures examined were benzene and carbon tetrachloride, benzene and ethylene dichloride, carbon tetrachloride and ethyl acetate, carbon tetrachloride and ethyl iodide, ethyl acetate and benzene, acetic acid and benzene, acetic acid and toluene, acetic acid and pyridine, pyridine and water, carbon disulphide and methylal, acetone and carbon disulphide, chloroform and acetone, ethylene dibromide and propylene dibromide. Margules has deduced the relation $d\log p_1/d\log x = d\log p_2/d\log (1-x)$, where p_1 and p_2 are the partial pressures, and x the concentration of liquid (1); for integration, the connection between p_1 and x is required, and the author employed the relation $p_1 = P_1 x e^{a/2} (1-x)^2 + b/3 (1-x)^3$ with a corresponding value for p_2 , P_1 being the vapour pressure of liquid (1). The values of p_1 and p_2 are so calculated, the constants a and b being obtained either from observations of the partial pressures of mixtures, or from the tangential values of the curve at the percentages 0 and 100. The calculated values so obtained are found to agree well with the observations, not only for mixtures of liquids of normal vapour density, but also for liquids of abnormal vapour density, and for mixtures in which chemical combination probably takes place.

L. M. J.

Vapour Pressure Relations in Mixtures of Two Liquids. III.

By A. ERNEST TAYLOR (*J. Physical Chem.*, 1900, 4, 675—689).—The author employs his previously recorded determinations (*Abstr.*, 1900, ii, 529) for the purpose of testing the validity of the van't Hoff-Raoult formula for the partial pressures in a mixture. The formula may be written $\log p/p_1 = c_2/c_1$, where p is the vapour pressure of one constituent, p_1 its partial pressure in the mixture in which its concentration is c_1 , c_2 being the concentration of the second component. The author finds that the partial pressure of acetone in mixtures of acetone and water is fairly well given by this expression if the concentration does not exceed 60 per cent., but that it does not hold for the partial pressure of the water. The author does not attempt to test Margules' expression, which has been found by Zawidzki to accurately yield the partial pressures in binary mixtures (preceding abstract).

L. M. J.

Influence of Neutral Salts on the Tension of Ammonia in Aqueous Solutions. By W. GAUS (*Zeit. anorg. Chem.*, 1900, 25, 236—264).—The tendency of a substance to form complex compounds may be regarded as a measure of its electro-affinity (Abegg and Bodlander, *Abstr.*, 1899, ii, 542). The author has therefore investigated the tendency of normal salts to form complex ammoniacal compounds, this being determined by the decrease of tension of ammonia in the aqueous solution, consequent on the addition of the normal salt. The vapour tension was measured in a manner essentially similar to that described by Gahl (*Abstr.*, 1900, ii, 389). For small tensions, it was found that the tension of ammonia was proportional to the concentration, and that between 23° and 27° the temperature coefficient could be regarded as linear. Various salts were added to the solution; it was found that sodium hydroxide and most

ammonium salts caused, as expected, an increase of tension, sodium and potassium chlorides also causing an increase. Ammonium nitrate, iodide, and thiocyanate, however, bring about a decrease of tension, the cause of this not being apparent, unless complex compounds are formed. All the other salts examined produced a decrease, which was most marked in the case of cupric and silver salts. Qualitatively, the results appear in accord with theory, but more extended data are necessary before the quantitative relations can be profitably discussed.

L. M. J.

Diagram of Freezing Point Depressions for Electrolytes. By JAMES G. MACGREGOR (*Trans. Nova Scot. Inst. Sci.*, 1900, 10, 211—235).—If α is the ionisation coefficient, and κ the depression constant, for an electrolyte whose molecule, as it exists in very dilute solution, contains p equivalents and dissociates into q free ions, then δ (equivalent depression) $= \kappa/p \cdot [1 + \alpha(q-1)]$. If for various electrolytes equivalent depressions are plotted against ionisation coefficients, the resulting curves must, at extreme dilution ($\alpha=1$), be tangential to the straight lines represented by the above equation, provided the proper values of κ , p , and q have been employed. A number of such curves have been drawn, based on the freezing point work of Arrhenius, Raoult, Loomis, Jones, Abegg, Wildermann, Ponsot, Archibald, and Barnes, and the determinations of ionisation coefficients at 0° due to Archibald, Barnes, Déguisne, and Whetham. The author concludes that the curves have positions, forms, and slopes such as they might be expected to have on reasonable assumptions as to mode of ionisation and constitution in solution, according to the van't Hoff-Arrhenius theory of the depression of the freezing point in electrolytic solutions. For all the electrolytes examined, the curves are consistent with the value 1.85 for the depression constant; in the case of potassium chloride, for which the best data are obtainable, the curve is not consistent with a greater limit of error than 0.01 in the value of the depression constant, unless improbable assumptions are made regarding the constitution of the electrolyte in solution.

J. C. P.

Distinction between Physical and Chemical Supersaturation of Liquids by Gases. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 131, 637—646).—The author applies the calorimeter to distinguish between those cases in which an abnormal quantity of gas is retained in a liquid by physical causes, and those in which the retention is due to the formation of some unstable compound. In the former case, the liberation of the excess of gas is always accompanied by a fall in the temperature of the liquid; in the latter there is, as a rule, a rise of temperature, because the unstable compounds in question are usually endothermic. The rise of temperature is observed in the decomposition of hydrogen peroxide in contact with spongy platinum, and in the reaction between hydrogen peroxide, potassium permanganate, and sulphuric acid, which with special precautions can be mixed so that very little oxygen is liberated, although the liquid becomes quite colourless. The retention of the oxygen in these cases is probably due to the formation of a hydrogen peroxide containing a higher proportion of oxygen than the dioxide.

C. H. B.

Viscosity of Gases as affected by Temperature. By LORD RAYLEIGH (*Proc. Roy. Soc.*, 1900, **67**, 137—139).—A continuation of the author's previous paper (Abstr., 1900, ii, 590), the gas examined being the residue from gases collected at the Bath springs, which was uncondensed by liquid hydrogen. It consisted chiefly of helium with, probably, some neon. The variation of viscosity between 100° and the ordinary temperature was the same as for hydrogen, so that the value of η (*loc. cit.*) is 0.681 as for hydrogen. Sutherland has deduced theoretically the expression $\theta^{\frac{1}{2}}/(1+c/\theta)$ as the function of temperature to which viscosity is proportional. The values of c obtained on the assumption of this expression are air, 111.3; oxygen, 128.2; helium and hydrogen, 72.2; argon, 150.2; the values for air and oxygen agree well with the values calculated by Sutherland from previous observations.

L. M. J.

Diffusion of Gold in Solid Lead at the Ordinary Temperature. By SIR W. C. ROBERTS-AUSTEN (*Proc. Roy. Soc.*, 1900, **67**, 101—105).—The author has previously shown that gold diffuses into lead at a temperature considerably below the melting point of the latter (Abstr., 1896, ii, 590). The experiments have now been extended to ordinary temperatures. Cylinders of solid lead with discs of solid gold affixed to their bases were kept for four years in a cellar at a temperature of about 18°. It was found that gold had diffused upwards, the concentration in the lowest layer of 0.75 mm. was about 1 oz. 6 dwt. per ton, and in a slice at a distance of over 7 mm. from the base gold was detected, the concentration being 1½ dwt. per ton. The great increase of diffusion with temperature is apparent from the fact that the rate here calculated is about 1/350,000 of that in molten lead. Experiments to test whether the diffusion is accelerated by the passage of an electric current have not yet led to conclusive results.

L. M. J.

Composition of the Vapour Phase in the System Water-Phenol, with One and Two Liquid Phases. By FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 1—11).—In the three-phase system water—phenol, the percentage of phenol in the vapour phase increases with rising temperature, and between 30° and 65° is less than that in either of the two liquid phases at the same temperature. [For the composition of the liquid phases compare Rothmund, Abstr., 1898, ii, 503.]

The author has investigated also the system with one liquid and one vapour phase, at the temperatures 56.3°, 75°, and 90°. At each temperature, a liquid containing a small quantity of phenol yields a vapour containing more, and one with much phenol yields a vapour containing less, phenol than itself. The vapour pressure and the amount of phenol in the vapour vary but slightly, while the composition of the liquid varies between wide limits. At each temperature, there is one mixture which is in equilibrium with a vapour of its own composition, and consequently has a maximum vapour pressure; the higher the temperature, the greater the proportion of phenol in this mixture.

The results are in agreement with the formula of van der Waals, $dP/dx_1 = P(x_1 - x_2)/[x_1(1 - x_1)]$, where P is the vapour pressure, x_1 and

x_2 the number of phenol molecules to 1 water molecule in the vapour and liquid respectively. J. C. P.

A New Conception of Thermal Pressure and a Theory of Solution. By G. N. LEWIS (*Zeit. physikal. Chem.*, 1900, 35, 343—368).—When two phases of a substance are in equilibrium, and the pressure on the one phase is increased, the pressure on the other phase must also be increased, if equilibrium is to be preserved; if dP_1 and dP_2 be these corresponding increments, then $dP_1/dP_2 = \sigma_2/\sigma_1$, where σ_1 and σ_2 are the specific volumes of the two phases. If ice and water are in equilibrium at atmospheric pressure, and the external pressure on the ice is increased by 1 atmosphere, equilibrium can only be maintained by an additional pressure of 1.09 atmospheres on the water, the ratio of the specific volumes of ice and water being 1.09. If each particle of a phase is regarded as having a tendency (expressed by the function ψ) to pass over into another phase, then the increase in ψ accompanying an increase in the external pressure P is proportional to the specific volume σ of the phase: or $d\psi/dP = K\sigma$. When β is the thermal pressure in the interior of a phase, and α is the resultant of all attractions or repulsions within the phase $P = \beta - \alpha$, so that $d\psi/d(\beta - \alpha) = K\sigma$. Hence the quantity ψ is affected only by a change in the difference $\beta - \alpha$, not necessarily by a change in the absolute values of β and α . For a liquid or solid in contact with its vapour, and under the condition that the vapour behaves as a perfect gas, the author deduces the equation $dP_1/P_1 = d(\beta_2 - \alpha_2)/(RT/v_2)$, where P_1 is the pressure of the vapour and v_2 the molecular volume in the liquid or solid phase; this means that the ratio of the change in vapour pressure to the total vapour pressure is the ratio of the change in external pressure to the pressure that would be exerted by the liquid or solid phase as a perfect gas. The author makes the supposition that the thermal pressure of a phase is equal to the pressure which the substance would exert if it existed under the same conditions as a perfect gas—that is, $\beta = nRT/V$, where n is the number of gram-molecules and V is the total volume. Further, all substances at the same temperature and under equal thermal pressure contain the same number of molecules in unit volume.

The author applies similar reasoning to the case of solutions, and shows that the above supposition is capable of interpreting the laws which hold in dilute solutions. Other consequences of the theory are discussed, particularly its relation to the theory of van der Waals.

J. C. P.

Velocity of Solution of Solid Substances. By LUDWIK BRUNER and STANISLAW TOLLOCZKO (*Zeit. physikal. Chem.*, 1900, 35, 283—290).—The authors have somewhat modified Noyes and Whitney's method (*Abstr.*, 1897, ii, 479), and worked with a number of other substances—benzoic acid, phenylacetic acid, phenylpropionic acid, acetanilide, and gypsum. A known amount of each, having been fused and cast in a regular shape, was rotated in water kept at a constant temperature, the rotation being sufficiently rapid to ensure the solution being uniform throughout. The results are in good agreement with the equation $dx/dt = K(C - x)$, where C is the concentration of the satu-

rated solution, x the concentration at time t , and K a velocity constant. The authors record the value of K/F , where F is the surface of the solid exposed to the solvent. These constants are diffusion coefficients, for the solid may be regarded as coated with a layer of saturated solution, and the whole process consists in a diffusion from this saturated solution to the surrounding unsaturated solution. The authors' arrangement is therefore a method of determining diffusion coefficients.

J. C. P.

Solid Solutions in Mixtures of Three Substances. By GIUSEPPE BRUNI (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 232—241).—Ternary mixtures are divided into the following six classes, conditioned by the capacity of the three components of forming solid solutions among themselves. (1) Two of the compounds, A and B are isomorphous, but C is not isomorphous with nor does it combine with either of the other two; (2) A and B are isomorphous, and each is capable of combining with C ; (3) A and B are isomorphous, and B alone combines with C ; (4) A is isomorphous with both B and C , but the two latter neither form a solid solution nor combine; (5) A is isomorphous with both B and C , and the two latter combine with one another; (6) the three components are all isomorphous. Triangular diagrams are given showing the saturation curves for the various cases.

T. H. P.

Inorganic Solvents and Dissociation Media. By PAUL WALDEN (*Zeit. anorg. Chem.*, 1900, 25, 209—226).—The author has investigated the solvent properties of a number of inorganic compounds, the dissociation in the solutions being determined by the conductivity method. Phosphorus trichloride and phosphorus tribromide are solvents for many organic compounds, and for the halogen compounds of arsenic, antimony, and tin, but most inorganic salts are insoluble in these liquids and no dissociation occurs. Phosphorus oxychloride dissolves many metallic salts and acids as well as organic compounds; binary salts undergo considerable dissociation, but tertiary salts and acids are only slightly dissociated. Arsenic trichloride is a good solvent for many salts, and also causes dissociation of binary salts. Sulphuryl chloride, SO_2Cl_2 , has slight dissociative power, which is, however, more marked in thionyl chloride, SOCl_2 , whilst sulphur dichloride, S_2Cl_2 , although a good solvent for many salts, causes practically no dissociation. Sulphur trioxide has no dissociative power, this result being interesting inasmuch as sulphur dioxide has been found to yield conducting solutions (Walden, *Abstr.*, 1900, ii, 10). Silicon tetrachloride and stannic chlorides are not good solvents and cause no dissociation; antimony pentachloride has no dissociative power, but antimony trichloride yields conducting solutions, a result in accord with the observations of Tolloczko (*Abstr.*, 1900, ii, 190). Bromine and boron trichloride have slight solvent, but no dissociative, power. The results appear to show that dissociative power cannot be ascribed to unsaturation, but is a specific property of the solvent, and it is noteworthy that all the dissociative solvents belong to the nitrogen or oxygen families.

L. M. J.

Solubility of Manganous Sulphate. By F. G. COTTRELL (*J. Physical Chem.*, 1900, 4, 637—656).—The solubility curves for the various hydrates of manganous sulphate were determined; the results as a whole are lower than those of Linebarger (*Abstr.*, 1893, ii, 417), a result probably due to inaccuracies in the latter's determinations. The author succeeded in preparing only the mono-, tetra-, penta-, and hepta-hydrates, but does not dispute the existence of the other hydrates found by Linebarger and others. The experimental methods, results, and the solubility curves are given; the latter indicate that from -10° to about $+8^{\circ}$ the heptahydrate is the stable form, the solubility increasing from about 48 parts to about 59 parts anhydrous salt per 100 parts of water. From about 8° to about 27° the pentahydrate is the stable form, the solubility increasing to about 66 parts per 100 of water; above 27° , the monohydrate is stable with a decreasing solubility curve. The tetrahydrate is not stable over any temperature range, its solubility curve cutting that of the heptahydrate at about 14° , and passing through the point of intersection of the curves for the monohydrate and pentahydrate. In each case, a considerable part of the labile portion of the curve was also determined. Incidentally, the author finds that a temperature of 170° is not sufficient to expel the last molecule of water from manganous sulphate; this occurs at 250° , and the salt may be heated to 300° without any decomposition.

L. M. J.

Soap Solutions. By A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 133—137).—Combination of the boiling point and vapour tension methods shows that solutions of sodium palmitate with less than 1 gram-molecule per 1000 grams of water cause an elevation of the boiling point and a decrease in the vapour tension, which starting from the concentration 0 must reach a maximum, to again become 0 at about a concentration of 1 gram-mol. per 1000 grams of water. This progressive change may be due to the part played by hydrolytic dissociation. A concentrated solution of sodium palmitate has the boiling point and vapour tension of pure water, so it is probably colloidal. Kahlenberg and Schreiner found that both dilute and concentrated soap solutions are good electric conductors. In the light of the author's experiments, this should be the case for dilute, but not for concentrated solutions (compare Krafft, *Abstr.*, 1899, ii, 470; Kahlenberg and Schreiner, *Abstr.*, 1899, ii, 202). J. C. P.

Hydration of Dissolved Substances. By WALTHER NERNST (*Chem. Centr.*, 1900, ii, 619; from *Nachr. k. Ges. Wiss. Göttingen*, 1900, 68—69).—Equilibrium in dilute solutions is independent of hydration, and no decision regarding the existence of hydrates can be obtained from observations thereon. Experiments on diffusion and on transference ratios should, however, give indications of hydration, and from the results of Lotmar, and of Garrard and Oppermann (following abstracts), the author concludes that hydrates are either non-existent, or present in only insignificant quantities.

L. M. J.

Hydration of Dissolved Substances. By H. LOTMAR (*Chem. Centr.*, 1900, ii, 619—620; from *Nachr. k. Ges. Wiss. Göttingen*, 1900, 70—85).—Experiments were made on the diffusion of silver nitrate,

and boric, butyric, and acetic acids in aqueous solution. It was found that the carriage of water with the dissolved substance was more than compensated by the opposing diffusion of water. L. M. J.

Hydration of Dissolved Substances. By C. C. GARRARD and E. OPPERMAN (*Chem. Centr.*, 1900, ii, 620; from *Nachr. k. Ges. Wiss. Göttingen*, 1900, 86—89).—The transference numbers were determined for hydrogen chloride, bromide, nitrate, and sulphate. Indications of migration of water with the anion were found, and on the assumption that the hydrogen ions are uncombined with water, the hydration of the anions is calculated, the compositions so obtained being $\text{NO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, $\text{Br} \cdot 4\text{H}_2\text{O}$, $\text{Cl} \cdot 4\text{H}_2\text{O}$, $\text{SO}_4 \cdot 11\text{H}_2\text{O}$. The authors consider that these results justify the statement that the hydration is in each case only slight. L. M. J.

Combustion of Gases. By SIMEON N. TANATAR (*Zeit. physikal. Chem.*, 1900, 35, 340—342).—The presence of 11—12 per cent. of propylene in electrolytic gas is sufficient to prevent explosion with the electric spark. When the percentage of propylene is a little lower, and explosion does take place, it is found that the hydrogen remains intact, whilst the oxygen is completely used up in the combustion of the propylene to carbon monoxide and water. Similar results are obtained with methane. The author does not think that the presence of 11—12 per cent. of propylene can lower the temperature of combustion of electrolytic gas below its explosion temperature. He thinks that, although the reaction $6\text{H}_2 + 3\text{O}_2 = 6\text{H}_2\text{O}$ liberates more heat than the reaction $\text{C}_3\text{H}_6 + 3\text{O}_2 = 3\text{CO} + 3\text{H}_2\text{O}$, the reaction velocity of oxygen with hydrocarbons is much greater than with hydrogen. J. C. P.

Reaction between Chloroform and Potassium Hydroxide. By A. P. SAUNDERS (*J. Physical Chem.*, 1900, 4, 660—674).—If, in the reaction between chloroform and potassium hydroxide, $\text{CHCl}_3 + 4\text{KOH} = 3\text{KCl} + \text{KCO}_2\text{H} + 2\text{H}_2\text{O}$, only 3 mols. of potash are primarily concerned, the reaction is quadrimolecular; if, however, the replacement of chlorine by hydroxyl proceeds in successive stages, the reaction is bimolecular. The author has hence determined the reaction velocity for various mixtures, and, although no high degree of accuracy is claimed for the determinations, yet they clearly show that, on halving the concentration of both reacting compounds, the velocity is reduced to one-fourth only, and that the velocity is proportional to the concentration of the potassium hydroxide solution, not to the cube of this concentration. The constant, also, calculated for the bimolecular reaction, varies far less than that deduced for a quadrimolecular reaction, so that the author is justified in considering that the replacement of the chlorine proceeds in successive stages. L. M. J.

Agreement between Chemical Formulæ and the Theory of Invariants. By P. GORDAN and WLADIMIR ALEXÉEFF (*Sitzungsber. phys.-med. Soc. Erlangen*, 1900; *Zeit. physikal. Chem.*, 1900, 35, 610—633).—If an atom is supposed to be divided into a number of parts equal to its valency, chemical formulæ may be represented as symmetrical products. Thus, when $\text{C} = c_x \cdot c_x \cdot c_x \cdot c_x = c_x^4$, $\text{H} = h_x$, and $\text{O} = o_x \cdot o_x = o_x^2$, propane is represented by $(c_1 c_2)(c_2 c_3)(c_1 h)^3(c_2 h)^2(c_3 h)^5$,

*tert.*butyl alcohol by $(c_1c_2)(c_1c_3)(c_1c_4)(c_2h)^3(c_3h)^3(c_4h)^3(c_1o)(oh)$, *p*-dichlorobenzene by $(c_1c_2)(c_2c_3)^2(c_3c_4)(c_4c_5)^2(c_5c_6)(c_6c_1)^2(c_1cl)(c_2h)(c_3h)(c_4cl)(c_5h)(c_6h)$.

On this basis, a far-reaching analogy is discovered between the conceptions, the processes, and the formulæ of chemistry and those of the invariant theory. The chief classes of chemical compounds are discussed from the point of view of this symbolical representation, and, in particular, the formula of indigo is so treated. J. C. P.

Inorganic Chemistry.

Origin of Atmospheric Hydrogen. By ARMAND GAUTIER (*Compt. rend.*, 1900, 131, 647—652).—The hydrogen in the atmosphere may be derived, not only from volcanic action and other well known sources, but also from the action of water on ancient granitic rocks at temperatures considerably below a red heat. Granite from the interior of a fairly large block, powdered in an atmosphere of carbon dioxide and afterwards heated with dilute acids at 100° or with water alone at 280°, yields a considerable quantity of gas, consisting mainly of hydrogen, together with hydrogen sulphide, ammonia, carbon dioxide, nitrogen, and traces of unsaturated hydrocarbons, and sometimes traces of methane. A granite from Vire when heated with phosphoric acid diluted with its own volume of water, gave 1400 c.c. of gas per kilogram and 916 c.c. of this was hydrogen. With water only at 280—300°, the proportion of gas liberated is smaller. The hydrogen and the ammonia that accompanies it are probably due to the action of the water on nitrides and chiefly on iron nitrides, although possibly some of the hydrogen may be derived from its action on carbides. C. H. B.

Higher Hydrogen Peroxides. By A. BACH (*Ber.*, 1900, 33, 3111—3118).—This paper is largely a reply to criticisms by Armstrong (*Proc.*, 1900, 16, 134) and Baeyer and Villiger (*Abstr.*, 1900, ii, 719) of a previous paper (*Abstr.*, 1900, ii, 470). Although Caro's acid when diluted does not reduce potassium permanganate, yet, undiluted, it rapidly decolorises a solution of the latter in concentrated sulphuric acid (permanganic oxide); the titration is sharply defined, and the whole of the oxygen of the persulphate is evolved together with that due to the permanganate. The view that a catalytic decomposition of the Caro's acid here occurs, appears to be excluded by the fact that the latter yields no oxygen either with manganous sulphate or with the liquid obtained after titrating Caro's acid with permanganic anhydride. The existence in Caro's reagent of a "higher persulphuric acid," $(\text{SO}_3\text{H}\cdot\text{O}\cdot\text{O}\cdot\text{SO}_3\text{H})_3$, is therefore assumed, which on dilution yields the acid, $\text{SO}_3\text{H}\cdot\text{O}\cdot\text{OH}$, incapable of reducing potassium permanganate. In the higher acid an ozonoid grouping is probable, since Caro's acid is formed on dissolving sodium dioxide in

well cooled sulphuric acid, although, on warming, ozone is evolved (compare Bamberger, *Abstr.*, 1900, ii, 536). W. A. D.

Action of the Silent Electric Discharge on Sulphur Perfluoride. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1900, [vii], 21, 205).—Sulphur perfluoride when submitted to the silent electric discharge remains unaffected, its stability under these conditions being comparable with that of the fluorides of boron and silicon; the gas is not absorbed by bromine, thiophen, or acid solutions of cuprous chloride. G. T. M.

Distribution of Sulphuric Acid in the Atmosphere. By HERMANN OST (*Chem. Centr.*, 1900, ii, 733; from *Chem. Ind.*, 23, 292—296).—In order to compare the quantity of sulphuric acid in the atmosphere at various places, rectangular pieces of cotton wool or floconné, 20 × 30 cm., saturated with barium hydroxide solution, were attached to the branches of trees in such a way that the material was kept taut and these were then left exposed for a considerable period. On the Süntel mountains, far from any commercial industry and where scarcely any coal is burnt, only 0.0555—0.180 gram of sulphur trioxide was found to have been absorbed in 153 days, whilst on the plain north of Hanover between Fuhrberg and Celle and 8 kilometres from the latter, 0.118—0.323 gram was absorbed in 193 days; the maximum amount was obtained by exposing the material in an open position unprotected on every side and away from trees, and the minimum in forests. In the neighbourhood of Hanover, 0.534—0.790 gram was absorbed in 175 days. Any sulphur present in mineral dust was excluded from the tests. E. W. W.

Persulphates. By RODOLFO NAMIAS (*L'Orosi*, 1900, 23, 218—223).—Persulphates rapidly absorb moisture from the air with the formation of the corresponding sulphate and sulphuric acid accompanied by the evolution of oxygen. Solutions of the persulphates are, however, very stable and may be employed in volumetric analysis for the estimation of substances having a reducing action. The best method of estimating the persulphates is to add excess of potassium iodide to a cold solution of the persulphate having a concentration not greater than 0.5 per cent. and after the liquid has remained for 10—12 hours, to estimate the free iodine by means of standard sodium thiosulphate solution.

In neutral solution, the persulphates have the power of dissolving many metals such as zinc, iron, and aluminium, the two normal sulphates being formed; copper is not attacked by neutral or acid solutions of the persulphates but is rapidly dissolved in presence of ammonia, under which conditions zinc and iron are slowly acted on. Silver undergoes gradual solution by either the acid or ammoniacal solution.

Chromium salts, in solutions either neutral or faintly acid with sulphuric acid, are quantitatively converted into chromic acid by excess of persulphate, a reaction useful in the estimation of chromium in steels, the chromium being first converted into chromate by means

of persulphate, the iron then separated by the addition of ammonia, and the chromate finally determined volumetrically.

By mixing ammonium persulphate and ammonium hydroxide with the solution of a manganese salt, complete precipitation of a hydrated manganese dioxide takes place, the oxidation being much easier and more convenient than when bromine is employed.

The oxidising action of persulphates in either acid or neutral solution can be made use of in the bleaching of such materials as textile fabrics, wood, and ivory, whilst when mixed with sulphuric acid they have the function of energetic depolarisers and may replace the nitric acid of the Bunsen cell.

When heated with a persulphate at 70—80°, ethyl alcohol is rapidly converted into aldehyde, whilst many organic compounds capable of oxidation, especially closed chain compounds, give up hydrogen and yields sulphonic derivatives. Thus quinol reacts with the persulphates, forming an insoluble sulpho-compound, and diaminophenol, *p*-phenylenediamine, *p*-aminophenol, &c., give characteristic colour reactions. On adding a persulphate to a cold solution of aniline hydrochloride, a dark green precipitate is formed, which is insoluble in water or alcohol and when treated with sodium hydroxide or carbonate solution turns dark green but remains insoluble.

T. H. P.

Action of Hydrogen Peroxide on Thiosulphates. By ARNOLD NABL (*Ber.*, 1900, 33, 3093—3095).—When hydrogen peroxide is added to a solution of sodium thiosulphate, a marked rise of temperature occurs and the solution becomes alkaline to litmus. This reaction is not due to liberation of sodium hydroxide, but to the formation of a new sulphur base, possibly in accordance with the equation $2\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}_2 = \text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_3 + \text{S}_2\text{H}\cdot\text{OH}$.

The new base is not volatile with steam, is insoluble in alcohol, and its aqueous solution has a strongly alkaline reaction and a green fluorescence. It precipitates the hydroxides of silver, copper, iron, and uranium from their salts, reduces hot Fehling's solution, and precipitates the sulphide from stannic chloride. It yields a platinichloride which is quickly reduced, especially on heating. The base probably possesses analogies with trimethylsulphine hydroxide and with hydroxylamine.

A. L.

Nitrogen Iodide. By OTTO RUFF (*Ber.*, 1900, 33, 3025—3029).—When iodine is added to liquid ammonia cooled to -60° , a black powder (possibly $\text{NI}_3\cdot\text{NI}_3$) is first formed, but eventually brownish-red plates with a greenish shimmer are obtained, which have the composition $\text{NI}_3\cdot 12\text{NH}_3$. At -35° to -40° , olive-green needles with the composition $\text{NI}_3\cdot 3\text{NH}_3$ are obtained; under diminished pressure, these lose ammonia and yield ordinary nitrogen iodide, $\text{NI}_3\cdot\text{NH}_3$ (compare Hugot, *Abstr.*, 1900, ii, 274).

When one atom of iodine is added to a mixture of 1 mol. of sodamide and liquid ammonia, cooled with liquid air, a violent reaction takes place; the product is a black compound, apparently of the composition Na_2NI_3 , in which the nitrogen is quinquivalent. On further addition of a second atom of iodine, or of 1 mol. of ammonium iodide,

one or other of the compounds $\text{NI}_3 \cdot 12\text{NH}_3$ and $\text{NI}_3 \cdot 3\text{NH}_3$ is formed, according to the temperature.

The cooling mixtures required were obtained by adding alcohol slowly to liquid air contained in a Dewar's beaker or in a beaker jacketed with cotton-wool, until the solidified alcohol redissolved to a syrupy liquid; when the temperature had risen to -70° , more liquid air and then alcohol were added as before, and the operation was repeated until enough of the mixture had been prepared. The substances prepared were filtered through glass wool and asbestos in a filter tube surrounded with the cooling mixture, which was contained in a Dewar's vessel. The washing was performed in the same tube, first with cooled liquid ammonia, then with cooled absolute ether.

C. F. B.

Formation of Nitric Acid during Combustions. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1900, [vii], 21, 145—201).—The experimental results embodied in these five memoirs have already been published (compare Abstr., 1899, ii, 648; 1900, ii, 475, 476, 538).

G. T. M.

Arsenic Triiodide. By R. DUPOUX (*Chem. Centr.*, 1900, ii, 836; from *Bull. Trav. Soc. Pharm. Bordeaux*).—A sample of officinal arsenic triiodide, consisting of a crystalline powder, when treated with water left a yellow, insoluble residue of antimony oxyiodide, SbOI , this compound being formed by the action of water on antimony triiodide contained in the drug. The insoluble residue from a second sample consisted of antimony oxyiodide and free arsenic, whilst a third sample left a residue of free arsenic alone. Another preparation contained an excess of free iodine and formed a clear brown solution which gradually became colourless. Arsenic triiodide should be tested by titrating with mercuric chloride, silver nitrate, or iodine solution; in the first case, the compound $\text{HgI}_2 \cdot 2\text{HI}$ is formed, whilst in the last two silver iodide and hydriodic acid are formed respectively.

E. W. W.

Constitution of the Perborates. By EMIL J. CONSTAM and J. CORA BENNETT (*Zeit. anorg. Chem.*, 1900, 25, 265—269).—The mode of preparation of the perborates and the fact that the ammonium salt contains $\frac{1}{2}\text{H}_2\text{O}$ appear to indicate a doubled formula for these compounds. The authors, however, find that the difference between the electrical conductivities at $v=1024$ and $v=32$ is 9.4 units, indicating a monobasic acid, so that the simple formula must be assumed. Attempts to produce a perborate by the electrolysis of orthoborates were unsuccessful, and hence did not confirm Tanatar's observations (Abstr., 1898, ii, 427).

L. M. J.

Reactions of Oxygen and Carbon Monoxide in the Presence of Alkalis. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1900, [vii], 21, 205—206).—After leaving a mixture of equal volumes of carbon monoxide and oxygen at the ordinary temperature for three months over a concentrated solution of potassium hydroxide, it was found that the former gas was absorbed by the alkali to form potassium formate, whilst the whole of the latter remained unchanged; a

similar result was attained in 14 hours by conducting the experiment at 100°. When ammonia is substituted for potassium hydroxide either at the ordinary temperature or at 100°, there is no formation of ammonium carbonate, and the absorption of carbon monoxide is very slight.

G. T. M.

Action of Sodammonium and Potassammonium on certain Metalloids. By CHARLES HUGOT (*Ann. Chim. Phys.*, 1900, [vii], 21, 5—87).—This memoir contains an extensive bibliography and a detailed account of the preparation of compounds previously described (compare Abstr., 1896, ii, 20; 1898, ii, 573; 1899, ii, 151, 650, 747; 1900, ii, 14, 274).

G. T. M.

Hydration Processes. By PAUL ROHLAND (*Ber.*, 1900, 33, 2831—2833. Compare Abstr., 1899, ii, 590).—It has been found that certain substances exert an influence on the hydration of Portland cement exactly similar to that which they have on the hydration of calcium oxide. Thus calcium chloride, aluminium chloride, and sodium carbonate accelerate, potassium dichromate, calcium chromate, boric acid, borax and potassium sulphate retard hydration, and sodium or lithium chloride has no action.

The same generalisations do not hold good for the hydration of calcium sulphate; in this process, sodium chloride, aluminium chloride, potassium dichromate, calcium chromate, and potassium sulphate accelerate, boric acid, borax and sodium carbonate retard hydration, and calcium chloride is indifferent.

The acceleration or retardation is roughly proportional to the concentration of the solution of substance employed. If the velocity of hydration is great, then the added substance has a greater influence, either accelerating or retarding, than when the velocity is small.

J. J. S.

Constitution of Hydraulic Cements. By ORAZIO REBUFFAT (*Gazzetta*, 1900, 30, ii, 177—182).—A correction of misquotations of the author's views on this question.

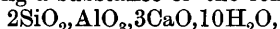
T. H. P.

Action of Sea-Water on Pozzuolana Mortar. By ORAZIO REBUFFAT (*Gazzetta*, 1900, 30, ii, 157—164).—The author's experiments lead to the following conclusions. 1. Sea-water transforms the cement of mortar made from pozzuolana into a hydrated aluminium silicate which contains small quantities of lime, magnesia, and the alkalis, and is perfectly stable towards the salts of sea-water. 2. Since pozzuolana mortar immersed in sea-water ultimately loses the whole of its lime, the employment of mixed mortars of cement and pozzuolana recommended by Michaelis cannot result in the fixation of the free lime of the cement.

T. H. P.

Artificial Pozzuolana. By ORAZIO REBUFFAT (*Gazzetta*, 1900, 30, ii, 182—190).—Experiments on artificial pozzuolana lead to the following conclusions. 1. Aluminium silicate of the composition $2\text{SiO}_2, \text{Al}_2\text{O}_3, 2\text{H}_2\text{O}$, when heated at 700—800°, loses water and assumes the nature of pozzuolana; the residue has not the power to take up again the moisture given off. It is to the presence of this silicate that

clay owes the pozzuolana properties it acquires on heating. 2. The silicate is not more easy of attack by hydrochloric acid after heating, although it becomes readily soluble in dilute alkali hydroxide solutions. 3. The compound $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ combines with lime in the presence of water, giving a substance of the composition



the formation of which determines the setting of pozzuolana made from kaolin or from clay heated at $700\text{--}800^\circ$. 4. This double silicate is readily decomposed by acids or by solutions of ammonium or magnesium salts, these salts removing the lime and leaving a hydrated aluminium silicate, $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, which in its chemical characters closely resembles certain varieties of the mineral halloysite. T. H. P.

Slow Action of Hydrogen Bromide on Glass. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1900, [vii], 21, 206).—When glass tubes containing gaseous hydrogen bromide are examined after two years, a portion of the gas is found to have disappeared and drops of its aqueous solution are formed, the water being probably derived from the slow action of the gas on the alkaline silicates and sulphates which enter into the composition of the glass. G. T. M.

Radio-active Lead and Radio-active Rare Earths. By KARL A. HOFMANN and EDUARD STRAUSS (*Ber.*, 1900, 33, 3126—3131).—Pure lead sulphate was isolated from pitchblende, the uranium micas, bröggerite, cleveite, and samarskite, which was radio-active although containing no trace of bismuth (polonium), barium (radium), titanium, thorium or uranium; the sulphate was insoluble in dilute sulphuric acid, but easily soluble in basic ammonium tartrate. The derived lead chloride crystallised from hot water, and then showed diminished radio-activity, whilst the crystals from the mother liquors showed increased activity. Only traces of radio-active bismuth could be isolated from pitchblende, the uranium micas and samarskite.

A mixture of cerium and yttrium oxalates, isolated from bröggerite, cleveite and samarskite, and freed from thorium and uranium, was found to be radio-active, the oxides derived therefrom being especially so. Uranosouranic oxide, U_3O_8 , from all the minerals already named, and also from euxenite, is always radio-active, and the same is true of the derived uranium oxalate, although on recrystallising the latter, the most soluble fractions are found to be inactive. Thoria from bröggerite, cleveite, and samarskite is active, although from euxenite, which is closely allied to samarskite in composition it is obtained inactive. W. A. D.

Formation of Mixed Crystals of Thallium Nitrate and Thallium Iodide. By C. VAN EYK (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 98—101).—The relation between the composition of mixtures of the fused salts and that of the mixed crystals deposited on cooling has been examined. The melting point line is of Roozeboom's type IV (compare Abstr., 1900, ii, 132), and rises immediately from the solidifying point of the nitrate, showing that mixed crystals are deposited from the melt. The mixed crystals deposited on solidification of mixtures with 0—9.9 molecular per cent. of the iodide are white; those from mixtures with more iodide are red. The white mixed crystals contain

from 0—8 molecular per cent. of the iodide, and the red from 65—100 per cent. Mixtures containing from 18—65 molecular per cent. of the iodide solidify at 215.5° to a conglomerate of the limiting mixed crystals. Thallium nitrate, which is rhombic at the ordinary temperature, is rhombohedral above 142° , but this transition temperature is lowered by admixture with the iodide; similarly, the transition point (169°) of the iodide is lowered by addition of nitrate. J. C. P.

Alterations in the Chemical Properties of Elements Produced by the Addition of Traces of Foreign Substances. By GUSTAVE LE BON (*Compt. rend.*, 1900, 131, 706—708).—When mercury is alloyed with traces of magnesium, it acquires the property of decomposing water, and becomes rapidly oxidised by exposure to the air at the ordinary temperature, a perceptible alteration being caused by the addition of only $1/14,000$ th part of magnesium. Magnesium contaminated with mercury rapidly decomposes water in the cold.

Aluminium foil, coated with a thin film of mercury, is quickly oxidised on exposure to air, and a strip of the metal placed vertically in a vessel containing water and mercury is continuously corroded at its lower end until completely disintegrated (compare Hunt and Steele, *Abstr.*, 1899, ii, 33). G. T. M.

Behaviour of Mixtures of Mercuric Iodide and Silver Iodide. By H. W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 84—86).—Investigation of fused mixtures of these salts shows that the melting point of mercuric iodide is lowered from 257° to 242° by an admixture of 14 molecular per cent. of silver iodide, whilst the melting point of silver iodide is lowered from 526° to 242° by an admixture of 86 molecular per cent. of mercuric iodide. The course of solidification shows that two kinds of mixed crystals are formed; on the mercuric iodide side, crystals of the rhombic mercuric iodide type with 0—4 molecular per cent. of silver iodide, on the other side crystals of the regular silver iodide type with 18—100 molecular per cent. of silver iodide. After solidification, mixtures containing from 4—18 molecular per cent. of silver iodide consist of a conglomerate of the two limiting mixed crystals. Those with 4 per cent. of silver iodide undergo a change at about 127° , because the mercuric iodide is transformed from the rhombic into the tetragonal form. When the mixtures with 18—100 molecular per cent. of silver iodide are cooled below 157° , the mixed crystals of the composition $\text{HgI}_2.2\text{AgI}$ are suddenly transformed into a compound of the same composition, the colour changing at the same time from pink to red. This temperature (157°) is comparable with the solidifying point of a chemical compound deposited from a liquid mixture. From mixed crystals containing less silver iodide than corresponds with the formula $\text{HgI}_2.2\text{AgI}$, the formation of the latter compound occurs at temperatures from 157 — 118° ; from mixed crystals containing more, at temperatures from 157 — 135° . The temperatures, 118° and 135° , are analogous to eutectic points, the conglomerates formed consisting of $\text{HgI}_2.2\text{AgI}$ with either HgI_2 or AgI . The temperature of transformation of regular silver iodide into the hexa-

gonal form is lowered by admixture of mercuric iodide from 157° to 135° ; the temperature of transformation of rhombic mercuric iodide into the tetragonal form is lowered by admixture of silver iodide from 127° to 118° . When the conglomerates of double salt with mercuric or silver iodide are further cooled to 45° , the double salt changes from red to yellow, whether it is pure or mixed with mercuric or silver iodide.

J. C. P.

Separation of Cerite Earths from Monazite Sand. By RICHARD JOS. MEYER and E. MARCKWALD (*Ber.*, 1900, 33, 3003—3013).—The crude material is the commercial 'cerium oxalicum oxydul pur,' which is obtained as a residue after the extraction of thorium from monazite sand; it contains 25 per cent. of water and gave 32.5 per cent. of cerium oxalate, 21.5 per cent. of didymium oxalate, and 14 per cent. of lanthanum oxalate. The oxalates are dissolved in nitric acid and separated as ammonium double nitrates. The cerium is precipitated as basic ceric sulphate from a solution of the mixed nitrates by adding ammonium persulphate and chalk (Witt and Theel, *Abstr.*, 1900, ii, 403), and is purified by dissolving in boiled nitric acid (nitric oxide reduces the ceric salt), separating as ammonium double nitrate, and recrystallising from nitric acid. The didymium and lanthanum salts in the filtrate from the cerium precipitation are separated (from ytterbium salts, &c.) by adding potassium sulphate to the boiling solution until it no longer shows the didymium absorption-spectrum; the double sulphates which separate can be dissolved by boiling with nitric acid and pouring into boiling water, and are purified by precipitating as oxalates; these are then dissolved in nitric acid, and the solution is boiled until free from acid. The separation of didymium from lanthanum is effected by adding magnesia until the solution no longer shows the didymium spectrum (Muthmann and Rölig, *Abstr.*, 1898, ii, 518); by repeating this operation twice and precipitating twice with oxalic acid and ammonia, the didymium is obtained nearly pure and free from all but a mere trace of lanthanum. The lanthanum is finally precipitated with ammonium oxalate in presence of ammonium chloride.

T. M. L.

Molecular Weight of Aluminium Compounds. By ELMER P. KOHLER (*Amer. Chem. J.*, 1900, 24, 385—397).—The molecular weights of the aluminium derivatives of acetylacetone and ethyl acetoacetate were determined by the boiling point method, carbon disulphide being used as the solvent, and found to accord respectively with the formulæ $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ and $\text{Al}(\text{C}_6\text{H}_5\text{O}_3)_3$.

Determinations of the molecular weights of aluminium bromide and iodide in the same solvent agree with the formulæ Al_2Br_6 and Al_2I_6 .

The molecular weights of the compounds of aluminium bromide with benzenesulphonic chloride and nitrobenzene, and of the compound of aluminium chloride with nitrobenzene, are shown by the same method to correspond with the formulæ $\text{Al}_2\text{Br}_6 \cdot 2\text{C}_6\text{H}_5 \cdot \text{SO}_2\text{Cl}$; $\text{Al}_2\text{Br}_6 \cdot 2\text{C}_6\text{H}_5 \cdot \text{NO}_2$, and $\text{Al}_2\text{Cl}_6 \cdot 2\text{C}_6\text{H}_5 \cdot \text{NO}_2$; in each case, it appears that 1 mol. of the aluminium haloid combines with 2 mols. of benzenesulphonic chloride or nitrobenzene to form 1 mol. of the product. It follows that the

addition of benzenesulphonic chloride or nitrobenzene to a solution of aluminium bromide of known boiling point should not affect the boiling point so long as the bromide is in excess; on the other hand, the addition of the bromide to a solution of benzenesulphonic chloride or nitrobenzene should immediately lower the boiling point, and the depression should be proportional to the quantity of bromide added; these conclusions were verified by experiment. A method is thus obtained for determining the changes which occur when an aluminium haloid is brought into contact with a given substance in an indifferent medium. The substance under investigation is added in successive portions to a solution of aluminium bromide of known concentration and boiling point until it is present in excess, and a further quantity of aluminium bromide is then added; the readings of the thermometer after each addition of material give an accurate account of what is taking place in the solution. By this means, it was found that the compounds of aluminium bromide with benzoyl chloride, benzophenone, and phosphorus oxychloride have respectively the composition $\text{Al}_2\text{Br}_6 \cdot 2\text{C}_6\text{H}_5 \cdot \text{COCl}$, $\text{Al}_2\text{Br}_6 \cdot 2\text{COPh}$, and $\text{Al}_2\text{Br}_6 \cdot 2\text{POCl}_3$. Acetophenone, benzenesulphonacetone, and ethyl benzoate form similar additive products with aluminium haloids; benzene and naphthalene, however, slowly react to form insoluble compounds, whilst pyridine and quinoline yield crystalline additive compounds also insoluble in carbon disulphide. An experiment with aluminium bromide and *p*-dibromobenzene showed that the non-applicability of Friedel and Crafts' reaction to dihalogen compounds is not due to a combination of the dihalogen compound with the aluminium haloid.

If one of the components of the additive compounds is present in large excess, dissociation occurs; thus, cryoscopic determinations of the molecular weights of aluminium bromide and chloride in nitrobenzene solution point to the formulæ AlBr_3 and AlCl_3 . Benzoyl chloride combines with aluminium bromide, in the absence of a solvent, to form a compound the molecular weight of which is shown by determination in carbon disulphide to correspond with that required for the formula $\text{Al}_2\text{Br}_6 \cdot 2\text{C}_6\text{H}_5 \cdot \text{COCl}$, whereas the determination in nitrobenzene gives an impossible value.

The conclusion of Werner and Schmujlow (*Abstr.*, 1898, ii, 214), that AlCl_3 is the only formula admissible for aluminium chloride is not justified, since they determined the molecular weight in pyridine, which combines with aluminium chloride to form a well crystallised compound.

E. G.

Cobalt Selenide. By HENRI FONZES-DIACON (*Compt. rend.*, 1900, 131, 704—705).—The selenide, CoSe , is obtained in an amorphous form by the action of selenium vapour on cobalt, and also by that of hydrogen selenide on heated cobalt oxide or chlorate.

The *sesquiselenide*, Co_2Se_3 , is produced by passing hydrogen selenide over cobalt chloride at moderately high temperatures; at lower temperatures, these substances react with the formation of friable grey *diselenide*, corresponding with the formula CoSe_2 ; this substance readily evolves selenium when heated.

The *selenide*, Co_3Se_4 , prepared by the interaction of hydrogen

selenide, hydrogen chloride, and cobalt chloride at a dull red heat, forms violet-grey, regular octahedra, the specific gravity at 15° being 6.54.

A *subseslenide*, Co_3Se , is obtained as a fused mass with a silvery lustre by reducing the preceding compounds in a current of hydrogen at a bright red heat; when this action is continued for some considerable time, the substance undergoes further reduction, but without yielding cobalt.

These selenides are only slowly decomposed by hydrochloric acid and by hydrogen chloride at high temperatures. Chlorine and oxygen displace selenium from the heated selenides, the action in the latter case giving rise to the formation of selenium dioxide and cobalt oxide. The selenides readily dissolve in bromine water containing excess of bromine.

Cobalt selenate, when reduced by hydrogen, yields either oxyselenides or a mixture of selenides and cobalt, according to the temperature employed. G. T. M.

Ammoniacal Cobalt Arsenates. By O. DUCRU (*Compt. rend.*, 1900, 131, 675—678).—The action of arsenic acid or an arsenate on solutions of cobalt salts containing ammonium salts and ammonia yields three insoluble ammoniacal cobaltous arsenates,

$\text{Co}_3(\text{AsO}_4)_2, \text{NH}_3, 7\text{H}_2\text{O}$,
 $\text{Co}_3(\text{AsO}_4)_2, 2\text{NH}_3, 6\text{H}_2\text{O}$, and $\text{Co}_3(\text{AsO}_4)_2, 3\text{NH}_3, 5\text{H}_2\text{O}$, formed from the hydrated arsenate, $\text{Co}_3(\text{AsO}_4)_2, 8\text{H}_2\text{O}$, by the partial displacement of water by an equal number of ammonia molecules. The composition of the product depends on the proportion of ammonia present, and is not affected by the proportion of ammonium salts. C. H. B.

Ammoniacal Nickel Arsenates. By O. DUCRU (*Compt. rend.*, 1900, 131, 702—704. Compare preceding abstract).—A solution containing a mixture of nickel and ammonium salts and free ammonia when treated with arsenic acid or a soluble arsenate, produces in the cold or on gently warming a gelatinous greenish-white precipitate which deepens in colour and becomes crystalline when the mixture is heated on the water-bath. The crystals are anisotropic and belong to the monoclinic system; they vary in composition according to the amount of ammonia present.

The octahydrated nickel arsenate, produced in the absence of ammonia, crystallises in needles and is identical in composition and crystalline form with the mineral annabergite. When the solution contains 1.38 per cent. of ammonia, a *monoammonionickel arsenate* is obtained; with 6.9 per cent. of this reagent, a *diammonio-salt* is formed, the corresponding *triammonio-compound* being precipitated in more concentrated ammoniacal solutions. These salts behave in a characteristic manner when heated at 155°, the composition of the compounds before and after heating being indicated in the following table:

| | |
|--|--|
| $\text{Ni}_3(\text{AsO}_4)_2, 8\text{H}_2\text{O}$. | $\text{Ni}_3(\text{AsO}_4)_2, 1\frac{1}{2}\text{H}_2\text{O}$. |
| $\text{Ni}_3(\text{AsO}_4)_2, 7\text{H}_2\text{O}, \text{NH}_3$. | $\text{Ni}_3(\text{AsO}_4)_2, 1\text{H}_2\text{O}, \frac{2}{3}\text{NH}_3$. |
| $\text{Ni}_3(\text{AsO}_4)_2, 6\text{H}_2\text{O}, 2\text{NH}_3$. | $\text{Ni}_3(\text{AsO}_4)_2, \frac{1}{2}\text{H}_2\text{O}, \frac{3}{2}\text{NH}_3$. |
| $\text{Ni}_3(\text{AsO}_4)_2, 5\text{H}_2\text{O}, 3\text{NH}_3$. | $\text{Ni}_3(\text{AsO}_4)_2, \frac{1}{2}\text{H}_2\text{O}, \frac{1}{2}\text{NH}_3$. |

The anhydrous arsenate, $\text{Ni}_3(\text{AsO}_4)_2$, is obtained in each case on heating the salt at dull red heat. G. T. M.

Periodic Phenomena in the Dissolution of Chromium in Acids. By WILHELM OSTWALD (*Zeit. physikal. Chem.*, 1900, 35, 204—256).—A continuation of the author's earlier paper (Abstr., 1900, ii, 730), in which the previous observations of periodicity by the dissolution of metals are fully discussed, and improvements on the apparatus employed by the author are described. An alloy of chromium and aluminium was employed and the effect of various compounds in bringing about regular periodicity investigated. It was found that dextrin has a remarkably powerful effect in this direction, other colloidal carbohydrates being active to a smaller extent. The periodic time increases as the action progresses and a number of experiments testing the regularity of this increase are recorded. Various curves obtained are given in the paper and further investigations are promised. L. M. J.

The System $\text{Bi}_2\text{O}_3\text{—N}_2\text{O}_5\text{—H}_2\text{O}$. By JACOBUS M. VAN BEMMELEN [and G. M. RUTTEN] (*Proc. K. Akad. Wetensch. Amsterdam*, 3, 196—203).—The various solid phases of this system have been examined. The normal salt, $\text{Bi}_2\text{O}_3, 3\text{N}_2\text{O}_5, 10\text{H}_2\text{O}$, has not a true melting point, but decomposes at 75.5° into a liquid and the basic salt $\text{Bi}_2\text{O}_3, \text{N}_2\text{O}_5, \text{H}_2\text{O}$. Two other normal salts with $4\text{H}_2\text{O}$ and $3\text{H}_2\text{O}$ respectively, have been discovered but not isolated; their composition has been deduced by means of Schreinemakers' graphical method. The basic salt, $\text{Bi}_2\text{O}_3, \text{N}_2\text{O}_5, 2\text{H}_2\text{O}$, is the first product of the action of cold water or dilute nitric acid (with less than 6 per cent. of N_2O_5) on the decahydrate, or of cold water on a not too acid solution of bismuth nitrate. It forms very thin, crystalline plates, without definite shape and showing double refraction; these cannot be dried over sulphuric acid without decomposition, and in contact with the mother liquor they are converted into another basic salt. The basic salt, $\text{Bi}_2\text{O}_3, \text{N}_2\text{O}_5, \text{H}_2\text{O}$, is formed from $\text{Bi}_2\text{O}_3, \text{N}_2\text{O}_5, 2\text{H}_2\text{O}$ when the latter remains in contact with a solution containing more than 1 per cent. of N_2O_5 ; the time required for its formation diminishes as the percentage of N_2O_5 rises. The crystals are monoclinic, but when the same salt is formed by the decomposition of the decahydrate at 75.5° , it has the form of thin, hexagonal prisms. The basic salt, $6\text{Bi}_2\text{O}_3, 5\text{N}_2\text{O}_5, 9(8)\text{H}_2\text{O}$, is formed at the ordinary temperature from $\text{Bi}_2\text{O}_3, \text{N}_2\text{O}_5, 2\text{H}_2\text{O}$, when the latter remains for some months in contact with a very dilute solution (less than 1 per cent. of N_2O_5 and less than 0.33 per cent. of Bi_2O_3); it is obtained also when the decahydrate is decomposed with water, and the solid salt which is formed is dissolved in much water. The crystals belong to the rhombic system; over sulphuric acid, they lose neither nitric acid nor water. The salt $2\text{Bi}_2\text{O}_3, \text{N}_2\text{O}_5, \text{H}_2\text{O}$ is the final product of the action of boiling water on the normal salt. The compounds $\text{Bi}_2\text{O}_3, 2\text{N}_2\text{O}_5, 2\text{H}_2\text{O}$ and $10\text{Bi}_2\text{O}_3, 9\text{N}_2\text{O}_5, 7\text{H}_2\text{O}$ are also described. The basic salts, $5\text{Bi}_2\text{O}_3, 4\text{N}_2\text{O}_5, 9\text{H}_2\text{O}$, $4\text{Bi}_2\text{O}_3, 3\text{N}_2\text{O}_5, 9\text{H}_2\text{O}$, $5\text{Bi}_2\text{O}_3, 3\text{N}_2\text{O}_5, 8\text{H}_2\text{O}$, and $5\text{Bi}_2\text{O}_3, 3\text{N}_2\text{O}_5, 6\text{H}_2\text{O}$, described by other investigators, are declared not to exist.

Isotherms, giving the composition of the liquid phases which are in

equilibrium with the different solid phases have been totally or partially determined for the temperatures 20° , 30° , and 65° . The isotherms have been graphically represented in equilateral triangles, and from these a figure in space has been drawn showing the conditions of equilibrium. The form of the triple lines in this system agrees with the form of those for the system $\text{HgO}-\text{SO}_3-\text{H}_2\text{O}$ (Hoitsemä, Abstr., 1896, ii, 15). J. C. P.

Egyptian Gold. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1900, [vii], 21, 202—204).—Analyses of Egyptian gold coins of the earliest epochs indicate that the material employed in their preparation consisted of argentiferous alluvial gold; only in later periods, from the time of Croesus onwards, does it appear that the metal was refined, the desilverisation process being that described by Pliny. Owing to the rarity of minerals yielding gold free from silver, it is possible, by analyses of the golden articles found in Egyptian tombs, to state approximately the epoch of their manufacture.

The gold leaf coverings of the mummies of the 6th and 12th dynasties contain 90—92 per cent. of gold, about 4 per cent. of silver, and 4—5 per cent. of organic matter, whereas those of the Persian epoch, ten centuries later, consist of nearly pure gold. G. T. M.

Certain Properties of Alloys of the Gold-Copper Series. By SIR W. C. ROBERTS-AUSTEN and T. KIRKE ROSE (*Proc. Roy. Soc.*, 1900, 67, 105—112).—The authors have investigated the freezing point curve for gold-copper mixtures. The freezing points of the pure metals are respectively, gold, 1063° ; copper, 1083° , and a minimum of 905° corresponding with an eutectic mixture was found for the alloy containing about 82 per cent. of gold, or 60 per cent. in atomic proportions. The atomic proportions of the eutectic mixture agree closely with those for the eutectic mixture of silver-copper, the freezing point curves also resembling one another closely. Microscopic examination was made of the various alloys, and these confirmed the existence of the eutectic alloy which makes its appearance even in the solidification of alloys containing only 27 per cent. of gold, as gold is comparatively slightly soluble in copper. Copper is, however, more easily soluble in gold than in silver, so that the character of rich gold-copper alloys is not very marked, the crystals closely resembling those of pure gold. L. M. J.

Mineralogical Chemistry.

Minerals of Roumania. By PETRU PONI (*Ann. Sci. Univ. Jassy*, 1900, 1, 15—148).—A complete and systematic description is given of Roumanian minerals, with notes on their occurrence at various localities. The paper is in French, and quotes much information and many analyses (some of which are given below) from the somewhat inaccessible Roumanian journals. Structural formulæ are discussed,

and several new analyses are given. Two new minerals are described under the names badenite and brostenite.

Pyrrhotite: an analysis (I) by Saligny, published in 1883, gives the formula $\text{Fe}_{18}\text{S}_{19}$. Copper-pyrites gave the results under Ia.

Badenite.—This is a massive mineral with a granular structure and steel-grey colour; sp. gr. 7.104. It occurs with chalybite, erythrite, and annabergite at Badeni, district of Muscel. From the analysis (II) it appears to be related to smaltite (or safflorite), but with part of the arsenic replaced by bismuth; formula $(\text{Co}, \text{Ni}, \text{Fe})_3(\text{As}, \text{Bi})_3$. Smaltite, also from Badeni, gave Saligny in 1883 the results under III (also CaCO_3 , 5.19; MgCO_3 , 1.46; insoluble, 4.99; manganese, trace).

| | S. | Cu. | Fe. | Co. | Ni. | As. | Bi. | Gangue. | Total. |
|------|-------|-------|-------|-------|------|-------|------|---------|--------|
| I. | 30.29 | 0.22 | 50.20 | — | — | — | — | 19.18 | 99.89 |
| Ia. | 33.96 | 33.57 | 32.02 | — | — | — | — | 0.20 | 99.75 |
| II. | 0.27 | — | 5.98 | 20.56 | 7.39 | 61.54 | 4.76 | — | 100.50 |
| III. | — | 0.33 | 12.26 | 21.93 | — | 52.43 | 0.67 | — | 100.30 |

Twenty-seven analyses are given of salt; besides sodium chloride, there are small amounts of magnesium chloride, sodium sulphate, calcium sulphate, water and insoluble matter. Analyses are also given of hæmatite, magnetite and limonite.

Brostenite.—This occurs abundantly as compact, friable, black masses in crystalline schists near Brosteni, district of Sucéva. It sometimes surrounds rhodochrosite, of which mineral it is evidently an alteration product. The three recalculated analyses (IV—VI) give the formulæ, $2\text{MnO}_2, \text{RO}, 2\text{H}_2\text{O}$, $3\text{MnO}_2, \text{RO}, 1\frac{1}{2}\text{H}_2\text{O}$, and $13\text{MnO}_2, 5\text{RO}, 12\text{H}_2\text{O}$ respectively. The mineral is therefore a manganite of iron and manganese, and is perhaps related to chalcophanite, $2\text{MnO}_2, (\text{Mn}, \text{Zn})\text{O}, 2\text{H}_2\text{O}$.

| | MnO_2 . | MnO . | FeO . | CaO . | MgO . | H_2O . | CaCO_3 . | Gangue. | Total. |
|-----|------------------|----------------|----------------|----------------|----------------|------------------------|-------------------|---------|--------|
| IV. | 52.40 | 6.16 | 11.47 | 3.05 | — | 11.97 | — | 14.75 | 99.80 |
| V. | 68.06 | 8.96 | 4.08 | 3.82 | 0.61 | 7.17 | 1.97 | 5.51 | 100.18 |
| VI. | 61.95 | 3.11 | 12.02 | 2.70 | 0.72 | 10.90 | — | 8.20 | 99.60 |

A white, saccharoidal, dolomitic limestone from Sucéva gave analysis VII; greyish-yellow crystalline chalybite associated with badenite gave VIII; yellowish, amorphous rhodochrosite associated with brostenite gave IX.

| | CaO . | MgO . | FeO . | MnO . | CO_2 . | Insol. | Total. | Sp. gr. |
|-------|----------------|----------------|----------------|----------------|-----------------|--------|--------|---------|
| VII. | 34.30 | 18.43 | — | — | 47.36 | 0.30 | 100.39 | — |
| VIII. | 4.46 | 7.21 | 40.72 | 6.12 | 39.49 | 2.21 | 100.21 | 3.455 |
| IX. | 4.07 | 2.30 | 3.17 | 50.29 | 39.02 | 1.42 | 100.27 | 3.193 |

Large crystals of augite gave anal. X by Murgoci (1895). Acicular crystals of tremolite from the dolomitic limestone of Sucéva (anal. VII) gave XI. Zoisite gave XII by Murgoci (1894). Analyses of serpentine, by Murgoci (1895), and of riebeckite (Abstr., 1899, ii, 768), are quoted.

| | SiO_2 . | Al_2O_3 . | Fe_2O_3 . | CaO . | MgO . | H_2O . | Total. | Sp. gr. |
|------|------------------|---------------------------|---------------------------|----------------|----------------|------------------------|--------|---------|
| X. | 45.82 | 37.46 | — | 14.20 | 4.16 | — | 101.66 | 3.232 |
| XI. | 58.22 | 0.92 | — | 13.37 | 25.33 | 1.76 | 99.60 | 2.937 |
| XII. | 36.49 | 34.19 | — | 24.81 | 3.67 | 2.91 | 102.07 | — |

New analyses of roumanite (Abstr., 1897, ii, 502 ; 1898, ii, 523) are given under XIII and XIV ; the first is of yellowish-brown material, and the second of material showing golden and greenish flashes. Seven analyses are also given of ozocerite (Abstr., 1897, ii, 502).

| | C. | H. | O. | S. | Ash. | Total. | Succinic acid. | Melting point. |
|-------|-------|-------|------|------|------|--------|----------------|----------------|
| XIII. | 80.04 | 9.76 | 9.13 | 0.83 | 0.24 | 100.00 | 3.2 | 310—312° |
| XIV. | 80.32 | 10.02 | 8.17 | 1.06 | 0.43 | 100.00 | 2.1 | 318—320 |

Numerous analyses are also given of mineral waters and of various naturally occurring saline substances, as well as of anthracite and lignite.

L. J. S.

Chemical Composition of Turquoise. By SAMUEL L. PENFIELD (*Amer. J. Sci.*, 1900, [iv], 10, 346—350).—The formula of turquoise is usually given as $2\text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, 5\text{H}_2\text{O}$, the copper, which is always present, being considered to be an accidental impurity ($2\text{CuO}, \text{P}_2\text{O}_5, 4\text{H}_2\text{O}$ according to Clarke, 1886) to which the colour of the mineral is due. A new analysis is given of pure material from the Crescent Mining District, Lincoln Co., Nevada ; this is of a beautiful robin's-egg blue colour, and breaks with a smooth fracture ; under the microscope, it appears to be homogeneous, and there is no evidence of the presence of two substances.

| P_2O_5 . | Al_2O_3 . | Fe_2O_3 . | CuO . | H_2O . | Insol. | Total. | Sp. gr. |
|--------------------------|---------------------------|---------------------------|----------------|------------------------|--------|--------|---------|
| 34.18 | 35.03 | 1.44 | 8.57 | 19.38 | 0.93 | 99.53 | 2.791 |

A consideration of this and other trustworthy analyses suggests that the copper is present as an essential constituent of the mineral ; and this is also supported by the fact that finely powdered turquoise dissolves in hydrochloric acid as a whole without discoloration. The new formula, $[\text{Al}(\text{OH})_2, \text{Fe}(\text{OH})_2, \text{Cu}(\text{OH}), \text{H}]_3\text{PO}_4$, represents the mineral as a derivative of orthophosphoric acid with the hydrogen atoms largely replaced by the univalent radicles $\text{Al}(\text{OH})_2$, &c. In some analyses, approximately two-thirds of the hydrogen atoms are so replaced, and the formula becomes $[\text{Al}(\text{OH})_2, \text{Fe}(\text{OH})_2, \text{Cu}(\text{OH})]_2\text{HPO}_4$.

L. J. S.

Analysis of the Thermal Waters of Achkel. By PUAUX (*J. Pharm.*, 1900, [vi], 12, 261—262).—These waters are very similar to those of Hamman-Lif and Bourbonne-les-Bains, and have an average temperature of about 44°. The greater portion of the salts present in the waters consists of sodium chloride, the rest consisting of calcium, magnesium and potassium sulphates, calcium chloride, and calcium carbonate.

H. R. LE S.

Physiological Chemistry.

Effect of Gestation on the Amount of Mineral Matter, especially Phosphoric Acid and Calcium, in Cow's Milk. By A. KORT (*Bied. Centr.*, 1900, 29, 667—668 ; from *Ing. Agr. Gembloux*, 1899, 453—475).—The percentage amounts of mineral matter, and especially of phosphoric acid and calcium, diminish more or less regu-

larly as the time of calving approaches, notwithstanding the decrease in lactation. Colostrum is rich in ash constituents.

During the period of the greatest flow of milk, the percentage amounts of phosphoric acid and calcium are lowest, whilst the total amounts are greatest. The amounts of mineral constituents gradually became normal as the production of milk diminishes, but again decrease towards the middle of the period of gestation.

Normal feeding has practically no effect on the amount of mineral matter in milk.

In the case of herbivorous animals, gestation has no effect on the amounts of phosphoric acid and calcium in the urine; feeding has the predominating effect. As regards carnivorous animals, however, the amount of phosphoric acid in the urine decreases during gestation.

N. H. J. M.

Division of Unfertilised Eggs. By ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1900, 4, 343—347).—The experiments were made on the eggs of *Arbacia*, and show that lack of oxygen, heat (32—33°), and exposure to ether, chloroform, or alcohol for a short time are all followed by karyokinetic nuclear division. The essential basis in all cases appears to be the production of localised areas of liquefaction in the protoplasm, and it is suggested that the centrosome normally plays the part of a liquefying enzyme.

W. D. H.

Influence of Digestion on Animal Heat. By EDWARD T. REICHERT (*Amer. J. Physiol.*, 1900, 4, 397—404).—Experiments on dogs show that the rise of temperature during digestion is due to increase of heat production. The maximum rise is during the fourth hour after a meal or later, but the changes in heat production (determined calorimetrically) and temperature are not proportional, for the greatest increase in heat production occurs during the first hour after feeding. The most marked effects are observed when the diet consists of proteid and fat, next with proteid, and least with fat.

W. D. H.

Gaseous Metabolism of the Submaxillary Gland. II. Absorption of Water. By JOSEPH BARCROFT (*J. Physiol.*, 1900, 25, 479—486).—The 'chorda blood' contains less water than the arterial blood. After the first minute of stimulation, the water lost from the blood exceeds in volume the saliva secreted, and may be measured by multiplying the volume of saliva by a factor the mean value of which is 1.12. In the first half minute of secretion, there is a large flow of saliva, followed in the second half minute by a relatively small flow. In the first half minute the absorption of water from the blood is large; this is diminished in the second half minute.

W. D. H.

Metabolism in Forced Feeding. By W. HALE WHITE and E. I. SPRIGGS (*Proc. Physiol. Soc.*, 1900, xxvii—xxviii).—Observations were carefully made on a woman for 56 days. If all the gain of weight had been proteid, the nitrogen corresponding to it would have been 441.8 grams. But as the nitrogen not accounted for in urine and fæces was 661.04 grams, 219 grams of nitrogen have to be accounted for in some other, at present unexplained, way.

W. D. H.

Metabolism in the Dog before and after removal of the Spleen. By DIARMID NOËL PATON (*J. Physiol.*, 1900, 25, 443—461).—After removal of the spleen there is a more rapid excretion of water after a meal, which probably indicates more rapid absorption. Otherwise there is no essential difference in the course or nature of the metabolism either during fasting or after feeding with the ordinary proteids of flesh, with vegetable food such as oatmeal, or with food rich in nucleins, such as thymus gland. W. D. H.

Absorption of Fat. By EDUARD PFLÜGER (*Pflüger's Archiv*, 1900, 82, 303—380).—Largely polemical. The main conclusion is that fat, like proteid and carbohydrate, undergoes hydrolytic decomposition before absorption, and is never absorbed as emulsified neutral fat. W. D. H.

Nutrition in Summer and Winter in Moderate Climates. By KARL ERNST RANKE (*Zeit. Biol.*, 1900, 40, 288—323).—Experiments on man show that within ordinary ranges of temperature there is no correspondence between a warm temperature and a necessarily more limited supply of food. In summer temperatures of over 20°, the instinctive lessening of appetite is related to pathological conditions induced by the excessive heat. W. D. H.

Properties and Origin of Lymph. By LEON ASHER and FREDERIC W. BUSCH (*Zeit. Biol.*, 1900, 40, 333—373. Compare Abstr., 1899, ii, 165).—The formation of urea from ammonium salts in the liver is accompanied by increased lymph formation: the lymph produced is more concentrated owing to increase of proteid. The formation of glycogen produced by injection of sugar into the portal system is accompanied by increase in lymph formation, but the concentration of the lymph remains constant. The intravenous injection of an assimilable proteid, such as casein, produces also a more abundant lymph which is richer in proteid. Heidenhain's lymphagogues of the first class cause increased liver activity and so lead to increased lymph formation; after intense activity of the liver, the coagulability of the lymph from the thoracic duct lessens. Activity of the pancreas similarly causes increase in lymph formation. These facts are all considered to support the view that lymph formation resembles the physiological process of secretion. W. D. H.

Formation of Glycogen after Feeding on Galactose. By ERNST WEINLAND (*Zeit. Biol.*, 1900, 40, 374—385).—In the rabbit, the administration of galactose leads to the formation of glycogen in the liver. W. D. H.

Urea Formation in the Body. I. Introduction. By WLADIMIR VON GULEWITSCH (*Zeit. physiol. Chem.*, 1900, 30, 523—532). **II. The Occurrence of Arginine in the Spleen.** By WLADIMIR VON GULEWITSCH and A. JOCHELSOHN (*ibid.*, 533—538).—A discussion on the relative importance of the processes of hydrolytic decomposition of nitrogenous matter in the body, and of oxidation in *intra vitam* urea formation introduces a series of papers. However important oxidation may be, there can be little doubt that hydrolysis occurs also in nitro

genous katabolism. Drechsel's well known work on the formation of urea from arginine *in vitro* renders it extremely probable that part, at any rate, of the urea formed in the body may pass through the arginine stage. Hitherto, although arginine has been found in plants, its existence has never been shown in the animal body, and the first step in the series of investigations shows it to be present in the spleen of the ox. Future papers will deal with its fate in the body.

W. D. H.

Lactase of the Pancreas. By ERNST WEINLAND (*Zeit. Biol.*, 1900, 40, 386—391).—The administration of milk increases the production of pancreatic lactase. Feeding on milk-sugar alone does the same thing. This is not due to the milk-sugar or any of its decomposition products passing into the pancreas; but the sugar acts as a stimulus, possibly to the secretory nerves of the organ.

W. D. H.

[**Lecithin in Brain and Milk.**] By ROB. BUROW (*Zeit. physiol. Chem.*, 1900, 30, 495—507).—The lecithin was extracted by means of an ether-alcohol mixture, and estimated from the amount of phosphorus in the extract. In different animals, it was found that the amount of lecithin in the milk varies, its proportion becoming greater as the relative brain weight of the animal increases. The following table gives the principal results:

| | Calf. | Dog. | Man. |
|--|-------|------|------|
| Relative brain weight | 1:370 | 1:30 | 1:7 |
| Lecithin of milk in percentage of } proteid | 1.40 | 2.11 | 3.05 |

W. D. H.

Relationship of Iron in the Urine and in the Blood. By ADOLF JOLLES and FERDINAND WINKLER (*Chem. Centr.* 1900, ii, 687—688; from *Arch. exp. Path. Pharm.*, 44, 464—476).—The daily excretion of iron in the urine averages 8 milligrams. The iron coefficient, that is, the proportion between the iron in the blood and urine, is 104.6 in health, but sinks in disease, and in anæmia gravis is only 7.2; here the excretion of iron is increased six-fold. In chlorosis, the excretion is normal, but the iron-coefficient falls.

W. D. H.

Diuretic Effects of Sodium Chloride. By WILLIAM H. THOMPSON (*J. Physiol.*, 1900, 25, 487—518).—The intravenous injection of small amounts of an isotonic solution of sodium chloride is followed usually by diuresis which is out of proportion to the volume of fluid injected. This is completed three or four hours after the injection. The excretion of urea and nitrogen is augmented, but the maximum occurs earlier than the maximum excretion of water. The diuresis is not caused by elevation of blood-pressure. A hydræmic condition of the blood is produced, but this is not the sole factor in producing the increased flow of urine. A diminution in the urinary chlorides is probably produced by the anæsthetic. The kidney volume corresponds in a general way to urinary outflow; but there are exceptions to this

rule. This is to be explained by the amount of lymph present. Bowman's theory explains urinary secretion better than Ludwig's.

W. D. H.

Diuretic Action of certain Purine Derivatives. By NARZISS ACH (*Chem. Centr.*, 1900, ii, 688; from *Arch. exp. Path. Pharm.*, 44, 319—348).—Dimethylxanthine acts on rabbits very markedly as a diuretic, and theophylline and paraxanthine are much more effective than theobromine. Of the monomethylxanthines, 4-methylxanthine acts as a diuretic, whilst heteroxanthine hardly acts in this way at all. Xanthine, isocaffeine, deoxycaffeine, and deoxytheobromine are not diuretics. The presence of methyl groups in the 4:6 and 1:6 positions appears to be of greater importance for diuretic action than in the 1:4 position.

W. D. H.

Action of Phloridzin on the Kidneys. By JULIUS VON KÓSSA (*Zeit. Biol.*, 1900, 40, 324—332).—In spite of what some observers have stated to the contrary, phloridzin does produce a nephritic condition. It also produces fatty infiltration of the liver and muscles. The nearly related pentoside, hesperidin, produces nephritis and albuminuria but not glycosuria.

W. D. H.

Physiological Action of certain Isomeric Hydroxyquinolines. By BÉLA VON FENYVESSY (*Zeit. physiol. Chem.*, 1900, 30, 552—564).—The two hydroxyquinolines, carbostyryl and kynurin, were investigated in rabbits and frogs. Administered by the mouth, the former causes paralysis by a curare-like action on the nerve-endings. The urine contains sugar, and after the removal of this by fermentation, is strongly lævorotatory; the substance to which this was due was crystallised out, and analysis of its potassium salt showed it to be carbostyryl-glycuronic acid. A part (about 25 per cent.) of the drug leaves the body as an ethereal sulphate. Two experiments were made in which the drug was given subcutaneously. One rabbit died; the urine of the other did not contain the optically active material.

Kynurin given by the mouth has no ill-effects on rabbits, but injected under the skin of frogs it produces much the same paralytic effects and heart-weakening as carbostyryl, although less marked in degree. The urine of the rabbits in this case also contains a lævorotatory material, which yields kynurin on decomposition. Elementary analysis of the crystalline material obtained from the urine shows that it is not a compound of glycuronic acid as anticipated.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Gaseous Exchanges between Plants and the Atmosphere. By TH. SCHLOESING, jun. (*Compt. rend.*, 1900, 131, 716—719. Compare Abstr., 1893, ii, 137, 180; 1894, ii, 110).—Comparative experiments, made on buckwheat and dwarf nasturtiums cultivated in media

freed from nitrifying organisms show that the plants, under these conditions, readily accommodate themselves to the substitution of ammonium salts for nitrates; buckwheat thrives slightly better on nitrates, whilst ammonium salts seem more favourable to the growth of nasturtiums. During the entire period of development, the plants evolve a volume of oxygen which is greater than that of the carbon dioxide absorbed. This excess of oxygen is derived principally from the reduction of the mineral salts extracted from the soil, and is very appreciably diminished when the nitrates are replaced by ammonium salts.

The quantitative results obtained in these experiments are exhibited in tabular form. G. T. M.

Assimilation of Free Atmospheric Nitrogen by Mycelia in the above-ground portions of Plants. By LORENZ HILTNER (*Bied. Centr.*, 1900, 29, 705—706; from *Centr. Bakt. Par.*, 5, ii, 831—832).—In 1897, A. E. Vogl discovered a fungus in the so-called hyaline layer of seeds of *Lolium temulentum*. The results of experiments made by the author in which *Lolium italicum* and *L. temulentum* were grown together in sand, with and without addition of potassium nitrate, indicate that in the case of *L. temulentum*, free nitrogen is assimilated.

It was not possible to separate completely the roots of the two varieties of *Lolium*. The results for the above-ground growth (in the pots without nitrate) are as follows (grams):

| | Dry matter. | N. |
|--------------------------------|-------------|--------|
| <i>Lolium temulentum</i> | 5.173 | 0.0304 |
| „ <i>italicum</i> | 0.974 | 0.0067 |

The amount of combined nitrogen in the seed and in the water given to the plants did not exceed 8 milligrams, whilst the roots of the two varieties together contained 7.8 milligrams of nitrogen. In the nitrate pots, there was a gain of 0.068 gram of nitrogen.

N. H. J. M.

Rôle of Oxygen in Germination. By PIERRE MAZÉ (*Ann. Inst. Pasteur*, 1900, 14, 350—368).—The failure of seeds to germinate under water is due to deficiency of oxygen. Whilst the seeds appear to be unchanged, they are in reality undergoing various changes; the hydrolysing diastases, and particularly zymase, are as active as in seeds germinating normally. On the other hand, the oxidations necessary for the elaboration of reserve foods being impossible under these conditions, the embryos remain inert.

Small seeds (cruciferous, for instance) may develop slowly at the expense of their internal atmosphere. Starchy seeds rapidly lose their germinating power, whilst oily seeds are more resisting. There is, however, no reason to suppose that any seeds are capable of resisting prolonged immersion in water.

The weakening of the vitality of submerged seeds is due to the production of toxic compounds, especially aldehyde.

The development of the plant at the expense of the reserve substances of the seed seems to depend on a certain number of diastasic actions,

the equilibrium of which cannot be disturbed without sooner or later causing death.

N. H. J. M.

Diffusion of Enzymes in the Seeds, with Special Reference to the Fat-decomposing Enzymes. By C. LUMIA (*Bied. Centr.*, 1900, 29, 669—673; from *Staz. sper. agrar. ital.*, 1898, 31, 353).—When the endosperm of growing plants was extracted successively with water and ether, the ethereal residue was found to be acid. Seeds similarly treated gave neutral residues. Fat is therefore decomposed in the endosperm during germination.

The results of experiments with *Ricinus communis* show that an aqueous extract of the germinating seeds liberated a considerable amount of acid from ricinus oil, which was added. When the extract was first boiled, the production of acid was comparatively small. Thymol was added in each case.

N. H. J. M.

Microchemical Examination of Aleurone-grains. By ALEXANDER TSCHIRCH and H. KRITZLER (*Chem. Centr.*, 1900, ii, 585—586; from *Ber. deut. pharm. Ges.*, 10, 214—222).—The aleurone-grains of the seeds of a variety of plants were found to consist mainly of globulins, similar to the globulins of animal proteids. The crystalloids contain at least two globulins of different solubility in 1 to 10 per cent. solutions of salts; they are insoluble in concentrated solutions of ammonium sulphate, sodium chloride (with a trace of acetic acid), and potassium dihydrogen phosphate, and either insoluble or sparingly soluble in concentrated magnesium sulphate solution. Aleurone-grains contain also, possibly, small amounts of albumoses.

The globoids contain protein (globulin), calcium, magnesium, and phosphoric acid; they dissolve in concentrated solutions of ammonium sulphate, acidified sodium chloride, and potassium dihydrogen phosphate, and are sometimes sparingly soluble and sometimes insoluble in concentrated magnesium sulphate solution.

The germinating power of seeds probably depends directly on the solubility of the crystalloids in dilute sodium chloride solution. The proteids in old seeds which are insoluble in 10 per cent. sodium chloride solution, but soluble in 1 per cent. sodium carbonate solution, correspond with Weyl's albuminates, and are not identical with Osborne's insoluble modification of globulin.

The oil of the seeds is not present as drops, but is mixed with the cell plasma; the gluten grains are free from oil.

N. H. J. M.

Dependence of the Production of Transitory Starch on Temperature and on the Action of Oxydases. By J. GRÜSS (*Bied. Centr.*, 1900, 29, 685—687; from *Woch. Brauerei*, 1899, 16, 519, and *Centr. Bakt. Par.*, 1899, 5, 775).—Sucrose is the first carbohydrate utilised in the germination of barley, the starch not being used until the embryo reaches a certain stage and is able to furnish the enzymes necessary for rendering the starch available. The rootlet is enclosed in a gum which probably consists of galactans; this contains a liquefying enzyme.

When a hole is bored through a potato the exposed surface soon becomes covered with cork. The latter contains two oxydases, an

α -oxydase and a β -oxydase. The α -oxydase is a carrier of free atmospheric oxygen and is destroyed by prolonged contact with alcohol, or by heating with alcohol for 15 minutes at 50–53°; it dissolves readily in glycerol, and is precipitated with only partial destruction by lead acetate. The β -oxydase liberates loosely combined oxygen. Neither the α - nor the β -oxydase is hydrolytic.

For detecting oxydases, paper soaked in an alcoholic solution of tetramethyl-*p*-phenylenediamine is employed; the dried paper, when moistened and placed on vegetable tissues containing oxydases, causes them to become coloured violet when exposed to air.

Barley contains a substance, *spermase*, which resembles oxydases, except in its extremely slight action on guaiacol; it is destroyed by heating with alcohol at 55–57°. As germination proceeds, the action of the spermase at first increases, then diminishes until it ceases. Probably the cessation is only apparent, the action being masked by reducing substances.

N. H. J. M.

Saps. III. By ALEXANDER HÉBERT (*Bull. Soc. Chim.*, 1900, [iii], 23, 839–842). Compare Abstr., 1896, ii, 494, and 1898, ii, 446).—A specimen of the sap or juice of the vanilla plant from the Congo was found to contain about 4 per cent. of crystallised calcium oxalate, to which the known irritant action of the juice is possibly due. Proteids and reducing substances are also present, but neither alkaloids nor fats could be detected.

N. L.

Plants Containing Zinc. By ERNST FRICKE (*Chem. Centr.*, 1900, ii, 769; from *Zeit. öffentl. Chem.*, 6, 292).—On a meadow near Ramsbeck, Westphalia, which is occasionally flooded by waste liquors containing zinc, and on soil near Bockwiese and Lautenthal which is known to contain zinc, a cruciferous plant very similar to *Arabis Halleri* has been found to flourish. In both cases, the plant contained zinc, and in the latter case the plant substance free from water and sand yielded 1.3 per cent. of ash which contained 0.94 per cent. of zinc.

E. W. W.

Oil and Fat of *Stillingia Sebifera*. By MASSIMO TORTELLI and R. RUGGERI (*Annali del Lab. Centr. delle Gabelle*, 1900, 4, 205–215; and *L'Orosi*, 1900, 23, 289–297).—The seeds of *Stillingia sebifera* contain 20.0 per cent. of fat and 19.2 per cent. of a very mobile, pale yellow oil, having the sp. gr. 0.9432 at 15°/15° and $[\alpha]_D - 3.41^\circ$ at 16°; the other chemical and physical constants have also been determined.

T. H. P.

Genesis of Terpenoid Compounds in Plants. By EUGÈNE CHARABOT (*Ann. Chim. Phys.*, 1900, [vi], 207–288).—A detailed account of work already published (compare Abstr., 1900, i, 363; ii, 101, 241, 361, 362; this vol., i, 38).

G. T. M.

Simultaneous Presence of Sucrose and Gentianose in Fresh Gentian Root. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1900, 131, 750–752. Compare Abstr., 1898, i, 349; Abstr., 1900, i, 511).—Fresh gentian root is shown to contain both sucrose and gentianose, the former being, perhaps, produced by the decompo-

sition of the latter sugar. Full details are given in the paper of the separation and identification of the sucrose. N. L.

Presence of Invertin or Sucrase in Grapes. By V. MARTINAND (*Compt. rend.*, 1900, 131, 808—810).—Invertin was found to be present in crushed grapes which, before maceration, had been carefully sterilised to destroy any enzyme which might be present on the outer surface of the skin. The amount of invertin present is sufficient to invert the whole of the sucrose present in the grapes. The invertin which is found in wine comes from the grape itself, and not from the enzyme which has produced fermentation in the wine. The invertin present in grapes is not so readily oxidisable as that obtained from other sources. It is absent from diseased wines, and from wines which have undergone strong oxidation. H. R. LE S.

Colouring Matter of Beetroot and its Absorption Spectrum. By JULIUS FORMÁNEK (*J. pr. Chem.*, 1900, [ii], 62, 310—314).—Beetroot contains an unstable colouring matter, which shows a yellow absorption band and, when warmed or kept, soon changes into the substance which exhibits the well-known blue and violet absorption bands. R. H. P.

Nitrogen in Peas. By WILHELM JOHANSEN (*Bied. Centr.*, 1900, 29, 717; from *Tidsskr. Landbr. Plant.*, 1899, 5, 100).—Nitrogen was determined in ten large and in ten small seeds. The following are the average results. Large seeds (450 mg.), $N = 3.35$; small seeds (226 mg.), $N = 3.17$. The average for all the seeds (338 mg.) was $N = 3.26$ per cent. There were only relatively few cases in which the small seeds had a lower, and the large seeds a higher percentage of nitrogen than the average of all the seeds. N. H. J. M.

Manurial Experiments with Hops. By THEODOR REMY (*Bied. Centr.*, 1900, 29, 664—665; from *Bl. Gersten-, Hopfen- u. Kartoffelbau*, 1899).—Experiments with hops in which farmyard manure was applied to soil not particularly deficient in humus-nitrogen decidedly increased the yield without having any marked effect on the quality of the hops. In the case of peat land (a typical East Prussian hop soil) containing 1.97 per cent. of nitrogen, the results showed that dung should only be employed in moderation, being injurious, rather than beneficial, as a source of nitrogen. N. H. J. M.

Cultivation of Olives. By FLAMINIO BRACCI (*Bied. Centr.*, 1900, 29, 673—675; from *Staz. sper. agrar. ital.*, 1899, 32, 161).—The different parts of the olive have the following percentage composition:

| | Water. | Organic matter. | N. | Ash. | K ₂ O. | Per cent. in Ash. | | | |
|--------------|--------|-----------------|-----|------|-------------------|--------------------|-------|---------------------------------|--|
| | | | | | | Na ₂ O. | CaO. | P ₂ O ₅ . | |
| Branches ... | 32.5 | 65.6 | 1.9 | 0.75 | 20.56 | 11.38 | 30.94 | 15.39 | |
| Leaves | 53.6 | 43.4 | 3.0 | 1.01 | 18.68 | 8.51 | 35.64 | 7.68 | |
| Fruit | 52.7 | 45.5 | 1.8 | 0.45 | 56.30 | 4.82 | 5.71 | 6.55 | |

It is estimated that the following amounts of manurial constituents are lost per hectare per annum (in wood, leaves, and fruit): N, 27.9; K₂O, 37.2; CaO, 13.9; and P₂O₅, 8.8 kilos. N. H. J. M.

So-called Invisible Injury [to Trees] by Smoke. By PAUL SORAUER and EMIL RAMANN (*Bied. Centr.*, 1900, 29, 678—685; from *Bot. Centr.*, 1899, 90, 50—56, 106—116, 156—168, 205—216, and 251—262).—Pine trees, 8—9 years old, in pots were subjected for an hour, in one case every day, and in others every second, third, or fourth day respectively, to the action of sulphur dioxide (0.0022 volume per cent. of the air) obtained by burning a mixture of carbon disulphide and alcohol. According to the frequency of the treatment, the amount of sulphuric acid in the needles was increased by 0.189, 0.112, 0.079, and 0.072 per cent. There was no visible change in the appearance of the needles either in the first or the second year; microscopical examination showed, however, that in many of the needles the chlorophyll substance had undergone changes or was completely destroyed.

Similar experiments were made in which the trees were subjected to the action of hydrogen chloride (0.00386 volume per cent.), obtained by burning a mixture of amyl chloride and alcohol. The amount of chlorine in the needles was appreciably increased, but the increase had no relation, as in the case of sulphur dioxide, to the frequency of the treatment. Less acid was, however, on the whole, absorbed by those plants which were rendered damp by spraying than by the others. Microscopic examination revealed no alteration in the chlorophyll substance. The stronger trees absorbed less acid than the weaker ones.

The results show that hydrogen chloride is less dangerous to pines than sulphur dioxide.
N. H. J. M.

Butter Fat. By ALPH. VAN ENGELER and P. WAUTERS (*Bied. Centr.*, 1900, 29, 666—667; from *Contrib. étude de la graisse du beurre, Brussels*, 1899, pp. 14).—Butter obtained at different periods was examined, as well as the butter from single cows. The rations of the cows included cotton seed meal or sesame cake.

The conclusion is drawn that abnormal butter fat may be produced at all times of the year, and that its formation does not depend on the feeding or on the period of lactation, but on physiological conditions not yet understood. In the authors' experiments, the Reichert-Meissl number varied from 23.3 to 38.5.

N. H. J. M.

Peat. By ARTHUR PETERMANN (*Bied. Centr.*, 1900, 29, 714—715; from *Bul. stat. agron. Gembloux*, 1899, No. 66, 11).—Peat from Herzogenwald was air dried, well mixed, and heated in an iron retort at about 450°. The following amounts of products were obtained from 1000 kilos. of air-dried peat: Coke, 337.5 grams; methyl alcohol, 600 c.c.; acetic acid, 3.058 grams; and tar, 57.675 grams. The tar yielded oil boiling at 0—100°, 100—200°, and 200—300°; 2.5, 12.75°, and 17.00 grams respectively; paraffin, 14.425; and coke, 11 grams. The yield of ammonia was 921 grams, and there was sufficient illuminating gas (from 2 kilos.) to burn with a good flame for 6 hours.

N. H. J. M.

Estimation and Composition of Humus and its Nitrification. By CHARLES RIMBACH (*J. Amer. Chem. Soc.*, 1900, 22, 695—703).—Humus, extracted in the usual manner, was precipitated with a mixture of calcium and magnesium sulphates. The humate (28 grams) was mixed with ignited sand (2 kilos.), which was then inoculated with soil extract and kept at about 25° for two months, water being added when necessary. It was then found that 5·94 per cent. of the humus nitrogen had become nitrified. When soils are extracted with dilute hydrochloric acid, a certain variable amount of humus is dissolved. The amount of nitrogen in the sodium hydroxide extract differs from that in the ammonia extract, and cannot be directly referred to the amount of organic matter in the latter.

In the usual process for determining humus, a certain amount of ammonia (about 5 per cent.) is included in the organic matter, making the results too high. Sodium hydroxide solutions extract more nitrogen than ammonia, and the question still remains, which of the two solvents is preferable. N. H. J. M.

Composition of the Coprogenic Mud of Kanger Lake in Livonia. By MAXIMILIAN GLASENAPP (*Bied. Centr.*, 1900, 29, 665—666; from *Baltische Woch.*, 1899, 40).—The mud is a light grey substance of the following composition (air dried): Water, 7·60; nitrogenous organic matter, 11·75; non-nitrogenous organic matter, 26·34; potassium, sodium, and calcium sulphates, 0·61, 0·66, and 2·67; calcium phosphate and carbonate, 0·37 and 15·86; magnesium carbonate, 5·33; ferric oxide and alumina, 2·88; silica and silicates, 25·93 per cent.

The mud can be obtained in large amounts in dry summers, and is locally useful as a manure. N. H. J. M.

Denitrification and the Action of Farm-yard Manure. By THEODOR PFEIFFER and OTTO LEMMERMANN (*Landw. Versuchs-Stat.*, 1900, 54, 386—462).—The utilisation of the nitrogen in the soil is hindered by an increase in the amount of organic matter as well as by denitrifying bacteria. Manuring with farmyard manure, dung, &c., not only increases the amount of organic matter but acts as a carrier of bacteria.

In pot experiments, the injurious effect of organic matter and denitrifying bacteria was only observed in the case of the first crop, but not afterwards.

When the amount of organic matter in the soil was increased by adding potassium citrate, or when pure cultures of denitrifying bacteria were added, there was a loss of nitrogen in the free state. In the case of farm-yard manure, the production of elementary nitrogen is quite unimportant as compared with other factors which give rise to incomplete utilisation of the nitrogen; this holds good even in pot experiments.

On light sandy soil the utilisation of nitrates is not affected by an application of 800 cwt. of old bullock or horse manure or fresh horse dung. In pot experiments, the same manure gave quite different results, but these have no direct bearing on practical agriculture.

The varying results obtained with different kinds of stable-manure

cannot be attributed either to the differences in the amounts of the different forms of nitrogen, and cannot be explained by denitrification and liberation of free nitrogen. The amounts of non-nitrogenous organic substances, especially xylan, had in these experiments no relation to the nitrogen assimilated. The differences observed would seem to be due to the various degrees of stability of the nitrogen compounds.

When farm-yard manure is improperly kept, the production of available forms of nitrogen may be entirely suppressed, even under conditions most favourable to the decomposition of the non-nitrogenous constituents. This is attributed mainly to the proteolytic ferments being injured, but requires further investigation.

The above conclusions are drawn from the results of a number of pot and plot experiments, which are fully described. N. H. J. M.

Analytical Chemistry.

Estimation of Ozone. By OTTO BRUNCK (*Ber.*, 1900, 33, 2999—3000).—A reply to Ladenburg (*Abstr.*, 1900, ii, 721).

T. M. L.

[**Estimation of Persulphates and Chromium.**] By RODOLFO NAMIAS (*L'Orosi*, 1900, 23, 218—223).—See this vol., ii, 15.

Estimation of Nitric Acid in Water. By N. N. KOSTJAMIN (*Chem. Centr.*, 1900, ii, 878—879; from *Pharm. Zeit.*, 45, 646).—Five c.c. of the sample are slowly mixed with a freshly prepared solution of 1 part of brucine in 3000 parts of sulphuric acid of sp. gr. 1.84 until a permanent rose coloration is formed. The greater the amount of nitrate the less of the reagent will be required. If nitrites should be present, these must be expelled by boiling with dilute sulphuric acid.

A table is given showing the number of c.c. of the reagent required for samples containing from one to twenty milligrams of nitric pentoxide per litre.

L. DE K.

Volumetric Estimation of Phosphorous Acid. By OTTO KÜHLING (*Ber.*, 1900, 33, 2914—2918).—Phosphorous acid may be estimated volumetrically by the aid of potassium permanganate solution but the reaction takes some time for completion. Zinc sulphate is added to the solution of the acid and the liquid is then heated on the water-bath and treated with permanganate solution. The zinc sulphate reacts with the alkali produced from the permanganate, yielding zinc hydroxide which carries down the manganese dioxide rapidly and completely. The titration is either carried out until the liquid remains permanently coloured for 10—15 minutes, or an excess of permangan.

ate is added, the liquid heated for 1—1.5 hours, and filtered, the precipitated manganese dioxide being then treated with potassium iodide and sulphuric acid and the liberated iodine estimated with thio sulphate. The excess of permanganate may also be estimated in the filtrate. A. H.

Destruction of Organic Substances by means of Chromyl Chloride in Toxicological Analysis. By C. PAGEL (*Chem. Centr.*, 1900, ii, 784; from *Pharm. Post*, 33, 489—490).—The apparatus consists of a tubulated retort fitted with a separating funnel and connected with a balloon which is in turn connected with two wash-bottles, of which the first is half filled with water and the second with a 1 per cent. solution of potassium hydroxide. The balloon is cooled by a thin stream of water. The finely divided, dried substance is put into the retort, 30—40 grams of a mixture of two parts of sodium chloride and one part of potassium dichromate are added for every hundred grams of material, and sulphuric acid is gradually introduced through the funnel. On heating, yellow fumes of chromyl chloride are evolved which carry over all the arsenic and most of the antimony and mercury. Altogether 40—50 c.c. of sulphuric acid are used and the heating is continued until the charred mass has become quite clear again. The residue in the retort may contain non-volatile metallic chlorides. The process seems a particularly delicate one for arsenic, and the author has found this to be a normal constituent of some parts of the animal body (spleen, brain, testicles, ovaries, &c.). L. DE K.

Flask for the Estimation of Carbon in Iron and Steel. By HEINRICH GÖCKEL (*Zeit. angew. Chem.*, 1900, 1034).—Koch (Abstr., 1895, ii, 86) has described an apparatus which, with slight modification by Ledebur, has become the recognised apparatus of the Society of German Iron Smelters. The author has made another slight modification to render it still more convenient.

In its new form, the apparatus differs from the previous one by having a wider ground neck into which fits the condenser through which passes a thistle funnel tube reaching to the bottom of the flask; the top of the neck of the flask is expanded, so that it can be filled with water to seal the apparatus after introducing the condenser. The side tube of the flask is placed somewhat higher than before. The acid mixture is poured through the funnel tube which is then sealed by means of a glass rod. At the lower end of the condenser is fitted a small slightly bent hook supporting a little glass bucket containing the sample; by a slight jerk this is made to drop into the acid. L. DE K.

Recognition of Barium Compounds as the Cause of Poisoning. By DIOSCORIDE VITALI (*L'Orosi*, 1900, 23, 260—263).—The detection of barium in the stomach contents or in the matter ejected by vomiting and the determination of the form in which it was administered may be carried out as follows. The material is first examined to see whether it gives a marked alkaline reaction, after which it is filtered and the residue extracted with boiling water so long as the latter becomes alkaline. If now the filtrate has an alkaline reaction and barium

carbonate is precipitated on passing carbon dioxide through it, the poisoning was brought about by barium oxide or hydroxide. If the addition of dilute sulphuric acid to the filtrate from the barium carbonate causes evolution of hydrogen sulphide and precipitation of barium sulphate, barium sulphide must have been taken. To detect barium chloride, nitrate, or acetate, the filtrate from the carbonate is evaporated to small volume and finely divided, pure lithium carbonate added until the liquid gives a persistent alkaline reaction, when it is boiled and filtered and the precipitate washed; the filtrate is evaporated to dryness on the water-bath, the residue extracted with a mixture of equal volumes of strong alcohol and ether, and the alcohol-etheral solution evaporated to dryness. The presence in the solid residue thus obtained, of lithium chloride, nitrate, or acetate shows that the corresponding barium salt was the cause of poisoning. In the event of barium carbonate having been employed, this will have been converted to a small extent into the chloride in the stomach, but as vomiting in general occurs soon after the administration of the barium salt, it will mostly remain as carbonate in the insoluble portion of the stomach contents, and may be detected by treating the latter with hydrochloric acid, which will cause evolution of carbon dioxide and the formation of soluble barium chloride. T. H. P.

Presence of Zinc in Alcohol. By THOMAS ROMAN and G. DELLUC (*J. Pharm.*, 1900, [vi], 12, 265—267).—When alcohol is stored in galvanised iron vessels, a small quantity of the zinc is dissolved.

A chloroform solution of urobilin serves as a very delicate test for zinc, with which it gives a green fluorescence, even when the merest trace of the metal is present. In making the test, it is necessary to mix the chloroform solution with $2\frac{1}{2}$ times its volume of absolute alcohol, in order to prevent the formation of an emulsion.

H. R. LE S.

Volumetric Estimation of Copper as Oxalate, with Separation from Cadmium, Arsenic, Tin, and Zinc. By CHARLES A. PETERS (*Amer. J. Sci.*, 1900, [iv], 10, 359—367).—The process is based on the fact that under certain definite conditions copper may be completely precipitated as normal oxalate. After being thoroughly washed on an asbestos filter, the precipitate may be treated with 5—10 c.c. of dilute sulphuric acid (1:1), diluted with a suitable quantity of water, heated to boiling and titrated with permanganate, or it may be dissolved in 10 c.c. of hydrochloric acid mixed with 0.5 gram of manganous sulphate and titrated with permanganate at 30—50°.

In order to ensure the complete precipitation of the copper, there should be present at least 0.0128 gram of its oxide in 50 c.c. of liquid, containing as nearly as possible 5 c.c. of strong nitric acid; two grams of oxalic acid will completely precipitate the copper after 12—16 hours. Ammonium nitrate interferes with the complete precipitation.

The process is not suited for the separation of copper from bismuth and antimony; cadmium, arsenic, iron, and small amounts of tin do not interfere. In the presence of zinc, the precipitate is slightly con-

taminated with zinc oxalate. Numerous test analyses are given in the paper. L. DE K.

Estimation of Tungsten in Ores. By FRIEDRICH BULLNHEIMER (*Chem. Centr.*, 1900, ii, 991—992; from *Chem. Zeit.*, 24, 870—871).—The following process is recommended for poor ores. 1—2 grams of the finely powdered sample are fused in a nickel crucible with 4 grams of sodium peroxide and 3 grams of sodium hydroxide, first over a very small and then over a full flame until the bottom of the crucible begins to glow. When the mass has solidified, the crucible is placed while hot in a beaker containing some water and the solution is then transferred to a 250 c.c. flask. If the liquid is coloured green by manganese, it is decolorised by means of hydrogen peroxide. When cold, the liquid is diluted to the mark, and half of the filtrate is mixed with 20 grams of ammonium nitrate. After any silica or stannic acid has deposited, magnesium nitrate is added to precipitate any phosphoric or arsenic acid. After 6 hours, the liquid is filtered, the precipitate washed with ammoniacal water and the filtrate made faintly acid with nitric acid. 20—30 c.c. of mercury solution (200 grams of mercurous nitrate heated with 20 c.c. of strong nitric acid and a little water and then diluted to 1 litre) are added, and after a few hours the liquid is nearly neutralised with ammonia. The precipitate is washed with water containing a little mercurous nitrate and then ignited and weighed. In the presence of much molybdenum, the precipitate should be mixed with ammonium chloride and then be reignited.

L. DE K.

Analysis of Tin and Tin-plated Wares. By V. MAINSBRECQ, (*Chem. Centr.*, 1900, ii, 743—744; from *Rev. intern. falsific.*, 13, 113—115).—Ten grams of the finely cut up sample are treated in an Erlenmeyer flask with strong hydrochloric acid and left overnight. Any undissolved matter, which may contain arsenic, antimony, and the bulk of the copper, is filtered off and treated with nitric acid, which converts the antimony into trioxide and dissolves the arsenic, which may be precipitated as ammonium magnesium arsenate. The hydrochloric acid solution is oxidised with nitric acid, neutralised with ammonia, again slightly acidified with hydrochloric acid, and precipitated with a strong solution of ammonium nitrate; the filtrate from the stannic hydroxide contains the lead and the remainder of the copper, which are precipitated as sulphides and then separated by the thiocyanate method. The filtrate contains zinc and iron, which are separated by means of ammonia, the zinc being finally weighed as sulphide. Tin and copper are, however, best determined in a separate portion. One gram is dissolved in nitro-hydrochloric acid, the tin precipitated by means of ammonium nitrate as directed, and the copper estimated in the filtrate either by potassium thiocyanate or colorimetrically. Tin-plate is simply dissolved in hydrochloric acid; copper is not likely to be present. L. DE K.

Sources of Loss in the Estimation of Gold and Silver in Copper Bars, and a Method for its Avoidance. By RANDOLPH VAN LIEW (*Chem. Centr.*, 1900, ii, 992; from *Eng. and Min. J.*, 69, 469, 498).—In order to minimise the loss of gold and silver in

the assay of copper bars, the following method is proposed. One or two assay tons of the turnings is dissolved in the cold in 350 c.c. of water and 100 c.c. of nitric acid of sp. gr. 1.42. After 18—20 hours, a further addition of at most 30 c.c. of acid must be made, and within 24—26 hours the solution will be completed. Any nitrous fumes are expelled by means of a current of compressed air in about 20—30 minutes; sodium chloride is then added. The silver chloride, mixed with the insoluble matter containing the gold, is collected on a filter, care being taken to wash it all down to the bottom. The cone of silver chloride is covered with 4—5 grams of assay-lead and with the filter heated at a temperature low enough to cause reduction of the silver chloride without any volatilisation of the chloride; cupellation &c., is then carried on as usual.

L. DE K.

Assay of Cupriferous Materials for Gold and Silver. By L. D. GODSHALL (*Chem. Centr.*, 1900, ii, 992—993; from *Trans. Amer. Inst. Min. Engin.*, Feb., 1900; *Berg.-Hüttenm. Zeit.*, 59, 454).—When applying the usual dry assay, care should be taken to examine the slags and the used cupel for traces of gold and silver. When the material is very rich in copper, it will be necessary to test for and estimate it in the weighed silver buttons.

The wet assay is best conducted as follows. The sample is dissolved in nitric acid and after being diluted with water, lead acetate and a corresponding quantity of sulphuric acid are added; the precipitated lead sulphate carries down any metallic gold, and after being dried, the precipitate is cupelled as usual. The filtrate is precipitated with a chloride or a bromide, and lead sulphate or bromide precipitated in the solution as before, and the resulting argentiferous deposit also cupelled in the usual manner.

The material may also be dissolved in nitric acid, evaporated with addition of sulphuric acid, and the resulting solution treated for a very short time with hydrogen sulphide. The precipitated copper sulphide carries down any gold and this is then recovered like the silver.

L. DE K.

Waters Contaminated by Cystine. By MARCEL MOLINIÉ (*Compt. rend.*, 1900, 131, 720—721).—The development of a yellow coloration by the action of the mercurichloride of sodium *p*-diazobenzene-sulphonate which is not destroyed by sulphurous acid cannot be taken as an indication of the presence of cystine in natural waters, because the same result is obtained with slightly acidified distilled water; on the other hand, the coloration is never produced in neutral solutions (compare Causse, *Abstr.*, 1900, ii, 457, 458).

G. T. M.

Estimation of Iodoform in Dressing Materials. By G. FRERICHs (*Chem. Centr.*, 1900, ii, 785; from *Apoth. Zeit.*, 15, 544. Compare Lehmann, *Abstr.*, 1900, ii, 372, 767).—One or two grams of the material are put into a 250 c.c. Erlenmeyer flask and 10—20 c.c. of alcohol or "spiritus æthereus" are added. Excess of *N*/10 silver nitrate and 10 c.c. of dilute nitric acid are then added, and after 15 minutes the excess of silver is titrated with *N*/10 potassium thiocyanate. Several

determinations should be made to see whether the iodoform is equally distributed over the whole of the material. L. DE K.

Estimation of Prussian Blue in Spent Gas Purifying Material. By A. O. NAUSS (*Chem. Centr.*, 1900, ii, 785—786; from *J. Gasbel.*, 43, 696—697).—Ten grams of the sample are repeatedly shaken in a half-litre flask with 50 c.c. of 10 per cent. sodium hydroxide. After 15 hours, the mixture is diluted to 505 c.c. and filtered. Fifty c.c. of the filtrate are added to 10 or 15 c.c. of a hot solution of iron alum (200 grams to 1 litre of water and 100 grams of sulphuric acid) and the whole is heated until the peculiar sweet odour has disappeared; the precipitate is filtered off and washed in a hot water funnel and then heated for a short time together with the filter with a definite volume of $N/50$ sodium hydroxide. The excess of alkali is then titrated with $N/50$ acid until a permanent pale greenish-yellow coloration is observed.

To estimate cyanogen in gases, 100 litres of the gas are passed through an absorption flask containing 20 c.c. of ferrous sulphate (1:10) and 20 c.c. of potassium hydroxide (1:3) and then through a second flask containing 10 c.c. of the mixture. The contents of the flasks are emptied into a half-litre flask, a little more potassium hydroxide and ferrous sulphate, and 1 gram of lead carbonate, to remove hydrogen sulphide, are added, and the whole is boiled for a few minutes. When cold, it is made up to 505 c.c. and 50 c.c. are titrated as directed. One c.c. of $N/50$ alkali = 0.0007794 gram of cyanogen. L. DE K.

Detection of Methyl Alcohol in Mixtures. By S. P. MULLIKEN and HEYWARD SCUDDER (*Amer. Chem. J.*, 1900, 24, 444—452. Compare Abstr., 1899, ii, 388).—Jandrier (Abstr., 1900, ii, 52) has recommended the use of gallic acid instead of resorcinol for the detection of methyl alcohol, since he found that the colour reaction of the former reagent with formaldehyde is much more delicate than that of the latter, and is less likely to be obscured by coloration occasioned by the simultaneous presence of other aldehydes.

The authors find that this modification of their test for methyl alcohol is inadmissible, since many other organic substances yield traces of formaldehyde on oxidation, which would not be detected by resorcinol but give the colour reaction with gallic acid owing to its greater delicacy. A number of precautions are mentioned which should be adopted before applying the resorcinol test, in order to remove substances from the solution which could prevent or obscure the appearance of the characteristic rose-red ring, and a method of applying the test in the presence of much ethyl alcohol is described in detail. E. G.

Colour Reaction of Alcohol. By R. GRASSINI (*L'Orosi*, 1900, 23, 224—225 and 297—298).—If a dilute solution of cobalt chloride, the concentration of which is not less than 0.5 per cent. and is best about 5 per cent., is mixed with potassium thiocyanate solution and a layer of alcohol is poured on to the liquid, which is then gently shaken so that the two strata do not mix, the alcohol assumes a beautiful azure-blue colour which is most intense at the surface of separation.

This reaction is not disturbed by the presence of nickel salts except when the ratio of cobalt to nickel is extremely small; the coloration, is, however, destroyed by hydrogen peroxide. If ether is used in place of alcohol, no coloration is obtained, so that the reaction may be used as a means of detecting the presence of alcohol in ether, which, if it contains 5 per cent. of added alcohol gives a marked coloration.

T. H. P.

Estimation of *m*-Cresol in Cresol Mixtures. By HUGO DITZ (*Zeit. angew. Chem.*, 1900, 1050—1052).—Raschig's process (Abstr., 1900, ii, 694) is not applicable when the mixture contains more than 10 per cent. of phenol. The sample should be suitably diluted with a mixture containing no phenol but a known quantity of *m*-cresol. In Raschig's process, the *o*-cresol and *p*-cresol are oxidised to oxalic acid; should this reaction be quantitative, it might prove of great value.

If, however, phenol is entirely absent, the author thinks that the assay may be more conveniently effected by the bromine process proposed by himself and Cedivoda (Abstr., 1900, ii, 54).

L. DE K.

Detection of Starch-Sugar in Wine. By ED. DELLE (*Chem. Centr.*, 1900, ii, 744; from *Rev. intern. falsific.*, 13, 131—132).—Tony-Garcin's process is recommended. One hundred c.c. of the sample are shaken with 30 grams of animal charcoal and, after 2 hours, filtered. Normally fermented wine then shows a rotation of about $+13^\circ$. If the decolorised wine contains less than 2 grams of reducing sugar per litre and has a rotation of more than $+13'$ before and after inversion, the presence of starch-sugar is proved. If more sugar is present, the test becomes uncertain.

L. DE K.

Estimation of the true percentage of Starch in Potatoes. By GEORG BAUMERT and H. BODE [with A. FEST] (*Zeit. angew. Chem.*, 1900, 1074—1078, 1111—1113).—After reviewing earlier processes, the authors have finally adopted the following method: 3 grams of the finely ground, air-dried potato are stirred at intervals in a porcelain beaker with 50 c.c. of cold water for an hour, the liquid is poured off as completely as possible through a small asbestos filter, and the latter returned to the beaker. Fifty c.c. of water are added, the beaker is closed with a lid and heated for three hours and a half in a Soxhlet digester at a pressure of 3 atmospheres. After cooling, the contents of the beaker are rinsed with 150—200 c.c. of boiling water into a 250 c.c. flask and boiled for 10 minutes; when cold, the liquid is made up to the mark and filtered. 100—200 c.c. of the filtrate are mixed with 10—20 c.c. of aqueous sodium hydroxide (100 grams per litre) and from the clear and stable solution, 25 c.c. are taken and mixed with 100 c.c. of commercial absolute alcohol, about 1 gram of fine asbestos being added in order to facilitate the separation of the starch. The precipitate is now collected on a Soxhlet asbestos filter-tube and washed by means of the suction-pump with 80 per cent. alcohol. The starch is then dissolved by means of about 3—5 c.c. of 5 per cent. hydrochloric acid, reprecipitated with 25—30 c.c. of commercial absolute alcohol and again collected on the filter; it is then

washed first with 80 per cent. alcohol, then with absolute alcohol, and finally with ether. After drying to constant weight at 120—130° in a current of air, the tube is weighed; it is then ignited in a current of air or oxygen and reweighed, when the loss represents the amount of starch. On account of the dilution caused by the alkali, it should be multiplied by 1.1.

In order to obtain the percentage of starch in the raw potatoes, the following formula is applied, $s = 100(v \times 1.1)/0.3 \times l/f$, in which f represents the weight of the raw potatoes, l the weight of the air-dried mass, and v the loss on ignition. Further experiments have conclusively shown that the loss on ignition really represents pure starch.

L. DE K.

New Process for the Estimation of Glycogen. By GEORG LEBBIN (*Chem. Centr.*, 1900, ii, 880—881; from *Zeit. öffentl. Chem.*, 6, 325—327).—Twenty grams of horse flesh or liver are treated in a porcelain dish with 90 c.c. of water and 10 c.c. of 15 per cent. potassium hydroxide and heated over wire gauze until completely dissolved, when the whole is evaporated down to 30—35 c.c. After diluting to exactly 50 or 100 c.c. and filtering through glass wool, 25 c.c. are mixed with 50 c.c. of a mixture of 90 parts of alcohol and 10 parts of 40 per cent. potassium hydroxide. The precipitated crude glycogen is left overnight, collected on a filter and washed with alkaline alcohol. The filter is perforated and the contents are washed into a 100 c.c. flask with 80 c.c. of boiling water. The flask is well shaken, and when cold the contents are neutralised with 10 per cent. hydrochloric acid using tincture of litmus as indicator. After adding 3—4 more drops of the acid, 5—10 c.c. of Brücke's reagent are added, the liquid diluted to the mark and filtered. Fifty c.c. of the filtrate are mixed with 75 c.c. of 95 per cent. alcohol, the precipitate is collected the next morning on a tared filter, and washed first with alcohol and then with ether. After being dried and weighed, the filter is burnt and any ash allowed for.

L. DE K.

Estimation of Acetic Acid. By V. DELFINO and M. MIRANDA (*Chem. Centr.*, 1900, ii, 1038; from *Mon. Sci.*, [iv] 14, ii, 696).—The solution of the acetic acid (? acetate) is boiled with an excess of ferric chloride. The resulting ferric acetate is decomposed into acetic acid and ferric hydroxide which then becomes anhydrous and adheres firmly to the sides of the beaker; it is dissolved in warm sulphuric acid, and reduced by means of a strip of silver foil. After removing the silver from the solution by means of hydrochloric acid, the iron is titrated as usual.

L. DE K.

Acidimetric Estimation of Protocatechuic Acid. By HENRI IMBERT (*Bull. Soc. Chim.*, 1900, [iii], 23, 832—834).—According to Massol (*Abstr.*, 1900, i, 600), protocatechuic acid crystallises in yellow needles melting at 199° and is neutralised by 1.5 mols. of alkali when phenolphthalein is used as the indicator. The author now describes experiments to confirm his former statement (*Abstr.*, 1900, i, 226), that protocatechuic acid is monobasic towards phenolphthalein, although

the end point is somewhat obscure. Moreover the acid employed was colourless, as it is usually stated to be, and melted at 194—195°.

N. L.

New Method for the Detection of "Saccharin" and Salicylic Acid alone or in presence of each other. By E. RIEGLER (*Chem. Centr.*, 1900, ii, 880; from *Pharm. Centr.-Halle*, 41, 563—564).—0.01—0.02 gram of "saccharin" is dissolved in 10 c.c. of water and 2 drops of 10 per cent. sodium hydroxide and put into a separating funnel. Solution of *p*-diazonitroaniline is added drop by drop with constant shaking until the greenish-yellow colour of the liquid has disappeared. After shaking with 10 c.c. of ether, the aqueous layer is removed, and 20—30 drops of 10 per cent. sodium hydroxide are added. At the place of contact between the ether and the soda, a fine green ring is formed; on shaking, the ether turns green and the alkali yellowish-brown. On removing the aqueous layer and adding 5 c.c. of strong ammonia, this turns a beautiful green, whilst the ether is decolorised. Under the same circumstances, salicylic acid first shows an intensely red ring, then a red aqueous but colourless ethereal layer which remains colourless when treated with ammonia, the latter turning red.

If 0.02—0.03 gram of a mixture of "saccharin" and salicylic acid is treated in the same manner, there is obtained first a red, somewhat brownish, ring, then a green ethereal, and a red aqueous solution; on addition of ammonia, a colourless ethereal and a violet ammoniacal layer. The colour of the latter varies in shade according to the respective amounts of the two substances.

The reagent is prepared by dissolving 2.5 grams of *p*-nitroaniline in 25 c.c. of water and 5 c.c. of sulphuric acid. Twenty-five c.c. of water and a solution of 1.5 grams of sodium nitrite are added, and the whole is diluted to the mark.

L. DE K.

Estimation of "Saccharin" in Beverages. By ED. DELLE (*Chem. Centr.*, 1900, ii, 744—745; from *Rev. intern. falsific.*, 13, 121—122).—In the absence of salicylic acid, 50—100 c.c. of the liquid free from alcohol are acidified with phosphoric acid and shaken with ether, or better with a mixture of ether and light petroleum. The ethereal liquid is evaporated, and the residue carefully fused with potassium hydroxide. The fused mass is dissolved in water, the liquid acidified with acetic acid, and the salicylic acid formed extracted with benzene. The weight of the salicylic acid multiplied by 0.77 equals the "saccharin." It may also be estimated colorimetrically by means of ferric chloride.

L. DE K.

Acidity of Milk. By PAUL VIETH and M. SIEGFELD (*Chem. Centr.*, 1900, ii, 922; from *Milch Zeit.*, 29, 593—597).—As the result of a long series of experiments, the authors state that the natural acidity of milk as found by titration with barium or sodium hydroxide with phenolphthalein as indicator is subject to serious variation. L. DE K.

Determination of the Specific Heat of Fats. By VANDEVYVER-GRAU (*Chem. Centr.*, 1900, ii, 923—924; from *Ann. Chim. anal. appl.*, 5, 321—323).—Pure tristearin has, at -6°, a fairly constant specific

heat of 0.336. This increases at 10°, 20°, 30°, and 40° to 0.397, 0.409, 0.449, and 0.501, and is at 50° 0.510. At 50° to 55°, the edges of small particles of tristearin begin to soften, and the specific heat quickly rises to 1.3—1.4. Palmitin shows a similar curve, the specific heat varying from 0.330 at - 7° to 0.478 at + 60°, and more than 1 at 3—4° below the melting point, 66.5°. Other fats behave in the same manner. The author considers the determination of the specific heat of fats, if not impossible, at least extraordinarily difficult, as the heat of fusion causes an elevation of temperature.

L. DE K.

Estimation of Fat in Finely Powdered Substances, particularly in Cocoa and Cocoa Mixtures. By P. WELMANS (*Chem. Centr.*, 1900, ii, 786—787; from *Zeit. öffentl. Chem.*, 6, 304—314).—Five grams of the material are put into a separating funnel and shaken with 100 c.c. of ether saturated with water for a few minutes; 100 c.c. of water saturated with ether are then added, and the whole is again vigorously shaken until a complete emulsion has formed. When the ether has sufficiently separated, 50 or 25 c.c. are pipetted off, the ether is distilled off, and the residual fat weighed. In calculating, it must be remembered that the total volume of the ethereal layer is not 100 c.c., but 100 c.c. *plus* the volume of the fat; the sp. gr. of cocoa fat may here be taken as 1.

Bonnema's tragacanth method (*Abstr.*, 1899, ii, 822) is also serviceable if due correction is made for the volume occupied by the fat.

L. DE K.

Absolute Iodine Absorption Number of Fats. By MASSIMO TORTELLI and R. RUGGERI (*Annali del Lab. Chim. Centr. delle Gabelle*, 1900, 4, 191—204; *L'Orosi*, 23, 109—122).—The authors ascribe the varying values obtained for the absolute iodine absorption number of one and the same fat by Wallenstein and Finck's method (*Chem. Zeit.*, 1894, 13, 1189—1191), to (1) the use of too small a quantity of material, and (2) a slight oxidation of the liquid fatty acids. These disturbing influences are avoided in the following process. Twenty grams of the oil or fat are saponified with alcoholic potassium hydroxide and afterwards converted into the lead soap, which is washed with 200 c.c. of hot (not boiling) water three times in succession, allowed to cool, dried between filter paper and heated in a reflux apparatus on a water-bath with 220 c.c. of ether for 20 minutes. The flask is then cooled in a mixture of ice and water, and maintained at a temperature of 8—10° for 2 hours, after which the liquid is filtered through a pleated filter into a 200 c.c. flask, made up to volume with pure ether, and the stoppered flask left all night in flowing water. The clear ethereal solution, filtered if necessary, is next removed to a separating funnel in which the soluble lead salt is decomposed by 150 c.c. of 20 per cent. hydrochloric acid; after vigorous shaking, the two layers are allowed to separate, and the lower aqueous liquor, together with the lead chloride, run off from the funnel. This is repeated with another 100 c.c. of the acid, after which the ethereal solution is washed twice with 150 c.c. of distilled water, filtered, and distilled until 40—50 c.c. remain. The residue is then placed in a 100 c.c. flask immersed to its neck in a water bath which is heated to boiling while

a current of carbon dioxide is passed through a narrow tube bent at a right angle and drawn out nearly to a point, and reaching almost to the bottom of the flask. After an hour's heating the flask is removed from the bath, and 8—15 drops (according as the oil contains more or less cotton seed oil or other drying oil), neglecting the first few, aspirated into a tared flask, and the iodine number determined in the usual way.

A large number of fats and oils have been examined by this method, the values obtained being greater, and nearer to the theoretical values, than those given by any process previously proposed.

T. H. P.

Solidification Point of Fatty Acids. By R. MORESCHINI (*Annali del Lab. Centr. delle Gabelle*, 1900, 4, 293—302. Compare Abstr., 1900, ii, 465).—The true solidifying point of a mixture of fatty acids obtained from soap may be found as follows. A test-tube 22—25 mm. wide is fixed by means of a stopper in a cylindrical glass vessel containing air having an initial temperature about 15° lower than the required solidifying point. About 20 grams of the mixed acids are fused and poured into the test-tube, the change of temperature being noted. As soon as the rate of cooling shows signs of slackening, the mass is subjected to vigorous stirring, this being kept up as long as the temperature continues to fall. After a time the mercury begins to rise and reaches a maximum at which it remains motionless for some two minutes; this maximum represents the true solidification point.

T. H. P.

Modification of Welman's Reaction. By THEODOR GEUTHER (*Chem. Centr.*, 1900, ii, 879—880; from *Zeit. öffentl. Chem.*, 6, 328—329).—The author prepares the reagent by pouring 25 c.c. of water on to 5 grams of powdered sodium phosphotungstate and then adding at once 30 c.c. of pure nitric acid of sp. gr. 1.39. This reagent keeps for about a year. To apply the test, 5 grams of the filtered lard are put into a tared test-tube, 3 grams of pure chloroform are introduced, and then 20 drops of the reagent. After thoroughly shaking, the tube is put aside and the coloration observed within two minutes; colorations forming after two minutes should be ignored. The presence of only 5 per cent. of vegetable oil betrays itself by a plain, dark-green coloration. A yellowish-green coloration may be due to stale or rancid lard.

L. DE K.

Brein's Reaction for Sesamé Oil. By ALB. J. J. VANDEVELDE (*Chem. Centr.*, 1900, ii, 783; from *Bull. Assoc. Belg. des Chimistes*).—A criticism of Brein's process (Abstr., 1899, ii, 824). Light petroleum should on no account be used in this test as it also gives the reaction, particularly if it has a high boiling point. It follows that the reaction is not due to nitrogenous matters as suggested by Breinl.

L. DE K.

Modification of Hübl's Method of Estimating the Acid and Saponification Numbers of Wax. By OTTO EICHORN (*Zeit. anal. Chem.*, 1900, 39, 640—645).—The difficulty of saponifying wax, especially Russian wax, may be obviated by dissolving it in amyl alcohol. For estimating the free acids, 6 grams of wax are covered

with 60 c.c. of pure amyl alcohol in a conical flask, and heated on an asbestos plate to boiling. Phenolphthalein is then added, and the titration made with $N/10$ alcoholic potash, which is added until the red colour disappears slowly. The liquid should be kept warm; enough to prevent separation of the wax, and the titration should be finished at about 60° , higher temperatures being avoided near the end to prevent risk of saponification. The acid values so obtained are lower than those hitherto accepted. For the saponification, 5 grams are dissolved in 60 c.c. of amyl alcohol, mixed with 25 c.c. of N alcoholic potash, the mixture gently boiled for half an hour, and titrated back with $N/2$ hydrochloric acid, after adding phenolphthalein. As soon as the solution has become colourless, the flask is heated until the liquid separates into two layers, and the addition of acid is continued until the lower, aqueous layer remains yellow even on long heating. A little water (10—25 c.c.) may be added to render the change more distinct. A blank experiment, conducted in the same manner, is indispensable. The presence of ceresin or paraffin does not interfere in any way. M. J. S.

Analysis of Fruit Essences. By GUIDO FABRIS (*Annali del Lab. Chim. Centr. delle Gabelle*, 1900, 4, 41—141).—A large number of experiments have been made on the methods of detecting the common adulterants of oil of lemons. The results show that there is no absolutely certain way of determining the presence of extraneous substances, although much can be learnt by the methods proposed by Schimmel & Co. and by Soldaini and Berté which make use of fractional distillation and measurements of specific rotation. Other tests such as colour reactions and determination of physical constants, which are useful in some cases, are also considered.

The addition of oils, resins, or balsams to oil of bergamot increases both its density and the residue left on evaporation, whilst oil of turpentine produces a diminution in the rotatory power and in the amount of esters. The admixture of lemon or orange oil with oil of bergamot increases its specific rotation and lowers its density, the amount of esters and the residue left on evaporation.

Methods for examining sweet and bitter orange oils and oil of mandarins are also referred to. T. H. P.

Valuation of Lemon Oil. By J. WALTHER (*Chem. Centr.*, 1900, ii, 903; from *Pharm. Centr.-H.*, 41, 585—588. Compare Abstr., 1900, ii, 173, and Schimmel & Co.'s *Geschäftsber.*, April, 1900).—In the author's method of testing lemon oil, the sodium hydrogen carbonate should be added to the mixture of lemon oil and hydroxylamine hydrochloride in fine powder, so that it is gradually dissolved during the digestion and decomposes the hydrochloride; 80 parts of the carbonate are required for about 70 of hydroxylamine hydrochloride. The end reaction with methyl-orange is described in the original paper and numerous analyses are quoted. E. W. W.

Estimation of Carvone in Ethereal Oils. By J. WALTHER (*Chem. Centr.*, 1900, ii, 970; from *Pharm. Centr.-H.*, 41, 613—616).—The quantity of carvone in ethereal oils is estimated by a method similar to that used for lemon oil (Abstr., 1900, ii, 173) 2—5 grams

of the oil are mixed with 10 grams of a freshly-prepared solution of hydroxylamine hydrochloride (2 : 3), 25 c.c. of alcohol free from aldehyde, and 2 grams of sodium hydrogen carbonate, and the mixture gently boiled for half an hour. To the cold solution, 6 c.c. of hydrochloric acid of sp. gr. 1.12 are added, the volume made up to 500 c.c., and the unused hydroxylamine determined in 25—50 c.c. of the filtered liquid. The standard solution of alkali should be free from carbon dioxide. Three samples of caraway-seed oil of sp. gr. 0.913 at 18°, 0.907 at 19°, and 0.893 at 15° were found to contain 52.5, 48.5, and 10.0 per cent. of carvone respectively; a curled-mint oil of sp. gr. 0.932 at 18° contained 51 per cent. and another of sp. gr. 0.887 at 20°, 16 per cent. of carvone.

E. W. W.

Acid and Saponification Numbers of some Copals. By WALTHER LIPPERT and H. REISSIGER (*Zeit. angew. Chem.*, 1900, 1047—1050).—The following varieties of copal have been tested; Angola copal, Angostura copal, Benguela copal, Brazil copal, Cameroon copal, Kauri gum, Dammara resin, and Madagascar, Zanzibar, Manilla, and Sierra Leone copals. The results have been duly tabulated.

The acid number is estimated by direct titration. One gram of the finely powdered copal is treated for a few hours with 10 c.c. of chloroform, 25 c.c. of alcohol are added, and the whole is gently warmed; if no solution takes place, a mixture of equal parts of ether and alcohol should be tried. Dichlorohydrin, which has been proposed as a universal solvent for resins, does not answer for copals. When cold, the acidity is taken with $N/2$ alcoholic potash using phenolphthalein as indicator.

The saponification number was estimated in the usual manner by heating with excess of standard alcoholic potash; the use of chloroform is, of course, excluded here. Henriques' cold saponification process does not work well with copals.

L. DE K.

Detection and Estimation of "Dulcin" (Phenetolecarbamide) in Articles of Food. By J. BELLIER (*Chem. Centr.*, 1900, ii, 822; from *Ann. Chim. anal. appl.*, 5, 333—337).—Lemonades or syrups, after dilution with water, are rendered alkaline with ammonia and shaken with ethyl acetate. In testing wine, 200 c.c. of the sample are treated with 2 grams of mercuric acetate and a little ammonia, and the filtrate is then shaken with 50 c.c. of ethyl acetate. When dealing with beer, 200 c.c. are mixed with 2—3 grams of sodium phosphotungstate and 10—20 drops of sulphuric acid, and the filtrate is shaken with 50 c.c. of ethyl acetate, after rendering alkaline with ammonia. In either case, the solution in ethyl acetate is evaporated to dryness and the residue dissolved in a little sulphuric acid and mixed with a few drops of strong solution of formaldehyde. On adding water, a flocculent precipitate is formed which after 24 hours may be collected, washed, dried, and weighed; its weight represents that of the "dulcin." It may be further identified by Jorissen's reaction.

L. DE K.

The Constituents of Digitalis and their Toxicological Detection. By DIOSCORIDE VITALI (*Chem. Centr.*, 1900, ii, 881; from *Boll. Chim. Farm.*, 39, 597—602).—When testing meat which had

been purposely poisoned with digitalis, the author was only able to detect digitoxin. The meat is extracted with dilute alcohol, the alcohol evaporated, and the residual liquid treated first with lead acetate and then with sodium sulphate. The filtrate, after being rendered alkaline with ammonia, is shaken with chloroform, and from this the digitoxin is precipitated by adding 20 times its volume of a mixture of 1 part of ether and 7 parts of light petroleum. After a further purification with alcohol and ether, the digitoxin gives the reaction with Keller and Kiliani's reagent very distinctly. L. DE K.

Isolation and Estimation of Colchicine. By ALBERT B. PRESCOTT and HARRY M. GORDIN (*Chem. Centr.*, 1900, ii, 784—785; from *Apoth. Zeit.*, 15, 521—522).—Twenty-five grams of powdered colchicum corm or seeds are extracted in a Soxhlet apparatus for 2 hours with 95 per cent. alcohol; the alcohol is distilled off, the oily residue rinsed with about 10 c.c. of hot water in a small separating funnel, and then shaken with 2—3 c.c. of light petroleum. After 15—20 minutes, the oily layer floats on the aqueous liquid. Without filtering, the latter is drawn off into a 100 c.c. flask, the stem of the funnel is rinsed with a little water, and the oily matter is again shaken with 10 c.c. of water. The whole is now put into a small dish, the light petroleum is removed by gently warming, and the contents are again transferred to the funnel and once more shaken with 2—3 c.c. of light petroleum; by this repeated treatment, the whole of the alkaloid is removed from the oil. The turbid aqueous solution is diluted to 100 c.c., 1—2 grams of talc are added, and after shaking it is passed through a dry filter.

The alkaloid may be estimated gravimetrically by first removing the water by means of a current of air, and finally drying the residue in a vacuum or over sulphuric acid. Volumetrically, it may be estimated by boiling it for 2 hours in a reflux apparatus with $N/40$ potassium hydroxide, and titrating the excess of the latter with $N/40$ hydrochloric acid. L. DE K.

Analysis of Quinine Glycerophosphate. By LÉON PRUNIER (*J. Pharm.*, 1900, [vi], 12, 309—312).—The phosphoric acid in quinine glycerophosphate cannot be estimated by calcination and subsequent oxidation with nitric acid, as the carbon produced during calcination reduces the phosphoric acid and a loss of phosphorus occurs. Quinine is not completely precipitated from quinine glycerophosphate by alkalis in the cold. The following method of analysis gives accurate results:—the quinine glycerophosphate is dissolved in dilute nitric acid (1:10), a solution of sodium hydroxide added and the precipitated quinine filtered off. The filtrate is boiled for some time, when the remainder of the quinine is precipitated and may be removed by extraction with ether or chloroform. The mother liquor from the ethereal or chloroform extraction is then mixed with a large excess of nitric acid together with 2—3 grams of potassium nitrate, evaporated to dryness and calcined to a white ash, care being taken that sufficient nitric acid is present to avoid the presence of any free carbon during calcination. The phosphoric acid present in the residue may then be estimated by any of the usual methods. H. R. LE S.

Analytical Chemistry of the Alkaloids. IV. Action of Bromine on Strychnine and Brucine. By KARL KIPPENBERGER (*Zeit. anal. Chem.*, 1900, 39, 609—627).—By acting on an acid solution of a strychnine salt with an excess of bromine water, a gradual substitution of bromine for hydrogen takes place; the monobromoderivative is formed almost instantly, in the course of an hour di- and tri-bromostrychnine are formed, whilst the substitution of more hydrogen atoms only takes place after several hours, and in the course of 12 hours 16—17 atoms of bromine are taken up, with formation of strychnine perbromide. The presence of sodium chloride greatly accelerates the reaction. Brucine salts behave in a similar manner.

When moderate amounts of potassium bromide are present, yellow, nearly insoluble, monobromostrychnine hydrobromide perbromide, $C_{21}H_{21}O_2N_2Br.HBr.Br_2$, is rapidly formed together with a little of the dibromo-compound; the presence of larger amounts of potassium bromide restricts the internal substitution. In no case could more than 2 atoms of bromine be introduced into the molecule.

Brucine forms a similar hydrobromide perbromide, but in consequence of its solubility in water, especially in the presence of acids, being greater than that of the strychnine compound, there is a greater tendency for the exterior atoms of bromine to effect substitution in the brucine molecule. The presence of both sodium chloride and potassium bromide favours the additive and hinders the substitutive reaction. The bromobrucine compounds exhibit a rose-red colour. However large the excess of bromine used, no perbromide containing more than two atoms of additive bromine could be obtained. M. J. S.

New Test for Gelatin and Isinglass. By OTTOMAR HENZOLD (*Chem. Centr.*, 1900, ii, 744, from *Zeit. öffentl. Chem.*, 6, 292—293).—Fruit jellies in which gelatin is suspected are boiled with water, the hot liquid is filtered, and a portion of the filtrate is mixed in a test-tube with an excess of solution of potassium dichromate (1:10). The mixture is again heated to boiling, then rapidly cooled and mixed with 2—3 drops of sulphuric acid. Gelatin gives a white, finely divided precipitate which becomes sticky after some time; vegetable jellies such as agar-agar, Iceland moss, and carrageen give no precipitate. L. DE K.

Artificial Silk and its Distinction from the Natural Product. By A. SOLARO (*Annali del Lab. Chim. Centr. delle Gabelle*, 1900, 4, 503—527).—Chemical and microscopical methods are given for distinguishing natural silk from the artificial preparations having a basis of nitrocellulose or gelatin. T. H. P.

Estimation of Humus. By CHARLES RIMBACH (*J. Amer. Chem. Soc.*, 1900, 22, 695—703).—See this vol., ii, 37.

General and Physical Chemistry.

Lamps for Spectra. II. By ERNST BECKMANN (*Zeit. physikal. Chem.*, 1900, 35, 443—458).—The paper contains a large number of practical details of the apparatus previously described (*Abstr.*, 1900, ii, 701). For the appreciation of these, reference must be made to the original, with its numerous illustrations. J. C. P.

Action of Heat on the Absorption Spectra and Chemical Constitution of Saline Solutions. By W. NOEL HARTLEY (*Sci. Trans. Roy. Dubl. Soc.*, 1900, 7, [ii], 253—312).—The author has examined the absorption spectra of nickel, copper, chromium, cobalt, uranium, and didymium salts, as well as that of potassium permanganate. The changes in the spectra accompanying dilution and rise of temperature were specially noted. The author's conclusions are summarised as follows. When a definite crystalline hydrate dissolves in a solvent which is not water, and is without chemical action on it, the molecule of the salt remains unchanged in chemical composition. In any series of salts which are anhydrous, and do not form well-defined crystalline hydrates, the action of heat up to 100° does not cause alteration in their absorption spectra, beyond that which is usual with substances which undergo no chemical change by such rise of temperature. The change is usually an increase in the intensity of the absorption, or a slight widening of the absorption bands. As a rule, crystalline metallic salts in which water is an integral part of the molecule dissolve in water at the ordinary temperature without dissociation of the molecule. Crystallised hydrated salts, dissolved in a minimum of water at 20°, undergo dissociation by rise of temperature. The extent of the dissociation may proceed as far as complete dehydration of the compound, so that more or less of the anhydrous salt may be formed in the solution. The most stable compound which can exist in a saturated solution at 16° or 20° is not always of the same composition as the molecule of the crystallised solid at the same temperature, since the solid may undergo partial dissociation from its water of crystallisation when the molecule enters into solution. Saturated solutions of deliquescent salts combine with water, when diluted, to constitute molecules of more complex hydrated compounds in such solutions. When a saturated solution of a coloured salt undergoes a great change of colour on dilution, or any remarkable change in its absorption spectrum due to the same cause, the dilution is always accompanied by a considerable development of heat.

J. C. P.

Dielectric Constants of Pure Liquids. By B. BERNARD TURNER (*Zeit. physikal. Chem.*, 1900, 35, 385—430).—The author has made an exhaustive study of Nernst's method of determining dielectric constants (*Abstr.*, 1894, ii, 437), and introduced several alterations. The various means of eliminating the external capacity are compared, and the use of that method recommended in which the capacity of the

trough employed is measured (1) with rod and condenser plate, (2) with rod alone. The ebonite lid of the trough is found to be a source of weakness, and is replaced by a glass lid of suitable construction. For exact measurements, the temperature coefficient of the apparatus must be taken into account. The standard condensers are enlarged and improved, whilst alterations in the compensation resistances are also described. With these improvements, it is possible to determine capacities five or ten times more accurately than with the older form of apparatus.

The dielectric constants of the following pure liquids have been very accurately determined: benzene, 2.288; *o*-nitrotoluene, 27.7; water, 81.1, all at 18°; these liquids may suitably be employed as standards. The dielectric constants of the following have been accurately determined, but either the liquids are more variable, or their purity has not been so thoroughly tested: ether, 4.368; aniline, 7.31; *m*-xylene, 2.376; nitrobenzene, 36.45, all at 18°. The dielectric constants of 16 other liquids and a number of temperature coefficients have also been determined.

J. C. P.

Influence of Non-electrolytes on the Conductivity of Electrolytes. By ARTHUR HANTZSCH (*Zeit. anorg. Chem.*, 1900, 25, 332—340).—The addition of carbamide, thiocarbamide, ethyl or methyl alcohol, ether, acetone, pyridine, urethane, or mannitol to aqueous solutions of the chlorides of the alkali or alkaline-earth metals diminishes the conductivity slightly, and to approximately the same extent. The addition of urethane or carbamide to solutions of silver nitrate produces a small diminution of conductivity, alcohol and mannitol have a rather larger effect, whilst thiocarbamide and pyridine have a very large effect. The addition of 2 mols. of pyridine to 1 of silver nitrate, for example, reduces the conductivity by more than 30 per cent.

The conductivity of ammoniacal solutions of ammonium chloride or calcium chloride is rather less than the sum of the conductivities of the solutions separately. The difference is somewhat greater in the case of ammoniacal solutions of silver nitrate. The latter contain the complex ion $\text{Ag}(\text{NH}_3)_2$, so that the mobility of this ion must be about the same as that of the simple ion Ag. The author considers that the results are best interpreted by Werner's theory (*Zeit. anorg. Chem.*, 1889, 3, 267).

T. E.

Decomposition-potentials of Fused and Solid Electrolytes. By CHARLES CORNFIELD GARRARD (*Zeit. anorg. Chem.*, 1900, 25, 273—312).—The salts are fused in hard glass tubes with electrodes of pure carbon. The currents produced by the application of a series of E.M.F.'s are observed and plotted in a curve. Each change of direction of this curve indicates the beginning of some decomposition. From the decomposition-potential (E) of a salt at the temperature T , and the temperature coefficient dE/dT , the heat of formation, Q , of the salt can be calculated by means of Helmholtz's equation, $Q = E - TdE/dT$. Where two decomposition points (E_1 and E_2) exist, two heats of formation may be calculated (Q_1 and Q_2). These are compared with the heat of formation determined by the calorimeter (Q).

The following table contains the principal numerical results:

| Substance. | Temp. | E_1 volts. | $10^4 \frac{dE_1}{dT}$. | E_2 volts. | $10^4 \frac{dE}{dT}$. | Heat of formation. | | |
|-------------------------|-------|-----------------|--------------------------|-----------------|------------------------|--------------------|---------|-------|
| | | | | | | Q_1 . | Q_2 . | Q . |
| NaI | 650° | 0.812 | | | | | | |
| KI | 674 | 0.833 | | | | | | |
| PbI ₂ | 470 | 0.435 | -7.7 | 0.728 | -6.2 | 46500 | 55000 | 44900 |
| PbCl ₂ | 669 | 0.80 | -8.9 | 1.238 | -8.0 | 75700 | 92200 | 75000 |
| CdCl ₂ | 563 | 0.715 | | 1.225 | | | | |
| CdBr ₂ | 591 | 0.62 | | 0.91 | | | | |
| CdI ₂ | 468 | 0.515 | | 0.681 | | | | |
| AgCl | 536 | 0.760 | -6.5 | | | 29800 | | 28100 |
| AgBr | 566 | 0.469 | -7.3 | | | 25000 | | 25300 |
| AgI | 564 | 0.348 | -6.5 | | | 20600 | | 18300 |
| AgI (solid) | 465 | 0.5 | | | | | | |
| ZnCl ₂ | 467 | | | 1.505 | | | | |
| ZnBr ₂ | 504 | | | 1.21 | | | | |

Lead Chloride and Iodide.—These salts are probably ionised as follows: $\text{PbI}_2 = \text{PbI} \cdot + \text{I}'$ and $\text{PbI} \cdot = \text{Pb} \cdot\cdot + \text{I}'$. The separation of the ions $\text{Pb} \cdot\cdot$ and I' from their charges will require one potential, that of the ions $\text{PbI} \cdot$ and I' another. Since PbI decomposes spontaneously into PbI_2 , and Pb when it is separated from its electric charge, it is obvious that this change is not reversible, and requires a higher potential than the reversible discharge of $\text{Pb} \cdot\cdot$ and I' ions. In accordance with this, the values of Q_1 agree well with those of Q for these salts. The first decomposition point is indistinct and not readily observed, whereas the second is well marked; it follows from this that the salts are mainly dissociated into $\text{PbI} \cdot$ or $\text{PbCl} \cdot$ ions. The results are quite similar to those obtained with water.

A saturated aqueous solution of lead chloride deposits Pb and PbO_2 at 1.568 – 0.002 t volts (with platinum point electrodes). A saturated aqueous solution of lead bromide gives Pb and Br at 1.306 volts (16°). The decomposition is the irreversible one through $\text{PbBr} \cdot$ ions.

With fused lead bromide, the results were untrustworthy owing to an increase of resistance at the anode; the curious behaviour of aqueous solutions of oxalic acid is shown to be due to a similar cause.

The saturated aqueous solution of cadmium chloride gives two decomposition points, showing that the electrolytic dissociation takes place in two stages.

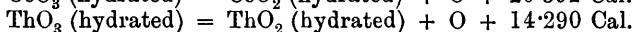
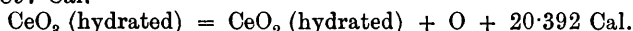
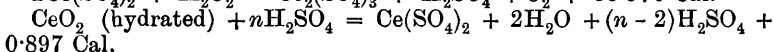
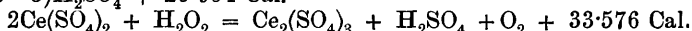
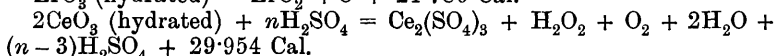
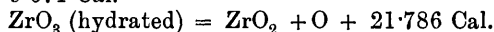
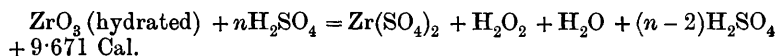
Cuprous chloride, when fused, conducts the current in accordance with Ohm's law, and shows no polarisation. T. E.

Model to Show Ionic Migration. By W. LASH MILLER and FRANK B. KENRICK (*Zeit. physikal. Chem.*, 1900, 35, 440–442).—Two horizontal cords, carrying cardboard riders at fixed distances to represent the ions and stretched by weights at one end, are made to move in opposite directions and with different velocities by means of pulleys to which the other ends of the cords are attached; the diameters of the pulleys are in the ratio 1 : 2 : 3. This model shows how the ions are separated at the electrodes, and how the concentration of the inter-

mediate solution is affected by the migration of the ions. The potential difference between the electrodes may be represented by the driving pressure on the pulleys, so that the apparatus serves to illustrate Ohm's law (compare Müller, *Abstr.*, 1900, ii, 643; Kohlrausch, *Abstr.*, 1900, ii, 712). J. C. P.

Determination of the Specific Heat of Fats. By VANDEVYVER-GRAU (*Chem. Centr.*, 1900, ii, 923—924; from *Ann. Chim. anal. appl.*, 5, 321—323).—See this vol., ii, 46.

Thermochemistry of the Hyperacids of Zirconium, Cerium, and Thorium. By L. PISSARJEWSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 609—627. Compare *Abstr.*, 1900, ii, 466).—The following heats of reaction have been determined:



The heats of solution of hydrated thorium peroxide (Th_2O_7) and oxide in dilute nitric acid are 34·368 and 29·893 Cal. respectively.

By dissolving zirconium peroxide in excess of hydrogen peroxide solution in presence of an alkali hydroxide, the *sodium* (with $9\text{H}_2\text{O}$) and *potassium* (with $9\text{H}_2\text{O}$) salts of perzirconic acid, $\text{H}_4\text{Zr}_2\text{O}_{11}$, were prepared but could not be obtained in a pure state. T. H. P.

Vapour Pressures of Aqueous Alcoholic Salt Solutions. By M. S. WREWSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 593—609).—The vapour pressure of a solution of potassium carbonate in a mixture of methyl alcohol and water is found to increase with the proportion of salt present. If P is the vapour pressure of the aqueous alcohol and P_1 that of the aqueous alcoholic potassium carbonate solution, the value of $(P_1 - P)/P$ diminishes as the temperature rises. Experiments made with salts of the alkali and alkaline-earth metals show that the change produced in the value of the vapour pressure of aqueous methyl alcohol when equivalent quantities of salts of the same acid are dissolved in it, increases as the molecular weight of the base of the salt increases, whilst salts of the same base with different acids produce effects which decrease as the avidity of the acid increases. Further, the changes produced in the vapour pressure of such solutions at any temperature by replacing potassium chloride by sodium chloride or potassium carbonate by sodium carbonate are identical; a similar relation holds for the replacement of potassium carbonate by potassium chloride and of sodium carbonate by sodium chloride. The system methyl alcohol—water—potassium carbonate separates into two layers (one containing excess of water and the other excess of

alcohol) which are found to have equal vapour pressures, that of the water being lowered and that of the alcohol raised by the presence of the salt.

T. H. P.

Vapour Pressure of a Series of Benzene Compounds. By ADOLF WINKELMANN (*Zeit. physikal. Chem.*, 1900, 35, 480—482).—A criticism of certain statements made by Woringer (see Abstr., 1900, ii, 709).

J. C. P.

Vapour Pressures of Binary and Ternary Mixtures. By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1900, 35, 459—479).—The greater part of this paper, dealing with the system water—phenol, has already been abstracted (this vol., ii, 9). The author has further investigated the three-phase system: water—aniline. The vapour in contact with the two conjugate liquids, aniline—water and water—aniline, has at temperatures from 41—90° a composition intermediate between those of the liquids. At 56.3° and 75°, the vapour from aqueous solutions of aniline contains more aniline than the liquid. The experimental results for the system water—aniline are shown to agree with van der Waals' formula (*loc. cit.*). The composition of the vapour phase of the system water—phenol—aniline, the liquid and solid phases of which have been previously investigated (Abstr., 1899, ii, 739; 1900, ii, 135), has been determined at 56.3°, in contact with two conjugate liquid phases.

J. C. P.

Theory of Chemical Catalytic Action. By HANS EULER (*Ber.*, 1900, 33, 3202—3206. Compare Abstr., 1900, ii, 532).—The author holds that a catalytic agent affects the dissociation of the substances primarily concerned in a reaction, and applies this to the hydrolysis of ethyl acetate. When K is the equilibrium constant of the reaction, and k and k' the velocity constants of the two opposite component reactions, then $K = k/k'$. The catalytic agent has no effect on the ratio k/k' , but alters the absolute value both of k and k' in the proportion $1 : 1 + kH$, where H is the concentration of the hydrogen ions yielded by the catalytic agent. Since the ratio k/k' is unaltered by the catalytic agent, the free energy of the reaction ($= RT \log_e k/k'$) is also unaltered.

J. C. P.

Most General Form of the Laws of Chemical Kinetics for Homogeneous Systems. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1900, 21, 693—786. Compare Abstr., 1900, ii, 199).—A theoretical paper, much of which is not suitable for abstraction. The author deduces general equations for the velocity of all kinds of reactions at constant volume in homogeneous systems. He discusses the form which the equation expressing the reaction must have, and the conditions which must be fulfilled in order (1) that the ratio of the velocities of two reactions which take place simultaneously is independent of the time; (2) that the concentration of a substance which is produced and decomposed in parallel reactions remains unchanged; (3) that the concentration changes of two substances are in a ratio to one another which is independent of the time. The form of the equation for reaction velocities with varying volume and (in the case of gases) with constant pressure is deduced, and the formulæ obtained are applied to

Bodenstein's experiments on the formation of water from hydrogen and oxygen (Abstr., 1899, ii, 733). J. C. P.

Sensitiveness to Light of Hydrogen Peroxide in Aqueous Solution on Addition of Ferro- and Ferri-cyanide. By WLADIMIR A. KISTIAKOWSKY (*Zeit. physikal. Chem.*, 1900, 35, 431—439).—When a few drops of potassium ferrocyanide are added to a 1 per cent. solution of hydrogen peroxide kept in the dark, the decomposition of the peroxide is very slow; if, however, the liquid is placed in direct sunlight, a brisk effervescence is observed in a few minutes, especially on shaking. It is shown that the liberation of oxygen from hydrogen peroxide under these conditions is in accordance with the equation: $k.t = \log a/(a-x)$, where k is a constant, a the initial concentration, and x the quantity of the hydrogen peroxide decomposed. The value of k when the reaction takes place in sunlight is 10—20 times greater than the value obtained when it takes place in the dark. It is not necessary that the liquid be illuminated the whole time; a minute's illumination is sufficient to accelerate the decomposition to the extent mentioned. It is shown that this acceleration is not due to a rise of temperature, but probably to a catalytic agent formed in the light from ferrocyanide and ferricyanide, an agent which is permanent even when illumination is discontinued.

J. C. P.

Absorption of Water Vapour by Chemical Compounds. By W. I. BUSNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 551—593. Compare Abstr., 1899, ii, 360 and 409).—9.7340 grams of aqueous sulphuric acid of the composition $H_2SO_4 + 2.285H_2O$, and 42.9056 grams of acid corresponding with the hydrate $H_2SO_4 + 0.338H_2O$ were placed under the same desiccator and the concentrations of the two determined from time to time. At the end of 787 days the respective compositions were $H_2SO_4 + 0.877H_2O$ and $H_2SO_4 + 0.648H_2O$; so that if interchange of water between two masses of aqueous sulphuric acid takes place in such a manner that one of them forms a hydrate containing less than $1H_2O$, the other will also give a hydrate with less than $1H_2O$. Next two masses of 0.8054 and 51.0118 grams respectively of the same acid of the composition $H_2SO_4 + 0.285H_2O$ were placed under a bell jar in vessels of the same sectional area so that equal surfaces were exposed to the air; it was found that the weights of water absorbed in the two cases were almost identical, the rate of absorption being independent of the composition of the acid between the limits $H_2SO_4 + 0.285H_2O$ and $H_2SO_4 + 2.038H_2O$. It was previously shown (*loc. cit.*) that the hydrate $H_2SO_4 + 4H_2O$ possesses a greater power of absorbing water than the hydrates immediately weaker and stronger than it; further experiments show that in this hydrate the affinity with which the water is held also has a maximum value. On exposing approximately equal quantities of phosphoric oxide and the hydrate $H_2SO_4 + 0.887H_2O$ together under a desiccator, it is found that the former absorbs more water than the latter. Other experiments with aqueous sulphuric acids show that hydrates containing between 12 and 12.5 or between 18 and 19 mols. of water per H_2SO_4

have greater powers of absorbing water than the adjacent lower and higher hydrates.

The absorption of water vapour by sodium sulphate has also been studied, as well as the interchange of water between the hydrated salt and aqueous sulphuric acid, when placed under the same desiccator. In the latter case, 3.7280 grams of $\text{Na}_2\text{SO}_4 + 11.654\text{H}_2\text{O}$ and 1.1742 grams of $\text{H}_2\text{SO}_4 + 0.274\text{H}_2\text{O}$ were employed, the composition of the hydrated sodium sulphate being, after successive periods of 24 hours : $\text{Na}_2\text{SO}_4 +$ (1) $11.654\text{H}_2\text{O}$ (initial value), (2) $7.80\text{H}_2\text{O}$, (3) $5.704\text{H}_2\text{O}$, (4) $4.345\text{H}_2\text{O}$, &c. The affinities of these hydrates for water are (1) 0.047, (2), 0.074 and, (3) 0.110, and (4) 0.162 respectively, these numbers increasing in a geometrical progression with constant ratio about 1.50. In the same way, the sulphuric acid absorbs water, forming at the end of each 24 hours hydrates which have affinities for water increasing in geometrical progression with a constant ratio about 1.50.

In the case of anhydrous potassium carbonate, the affinities of the various hydrates for water increase geometrically with a ratio of about 1.40. Experiments were also made on the removal of water from aqueous potassium carbonate by means of sulphuric acid placed in the same desiccator.

Anhydrous sodium nitrate absorbs water vapour, yielding after successive intervals of 24 hours hydrates which have affinities for water nearly equal in value. When the water is removed from the hydrated nitrate by placing it together with sulphuric acid under a desiccator, the hydrates obtained at the end of each day's exposure have affinities for water of the values 0.077, 0.112, and 0.349 respectively, there being in this case no constant ratio. Similar experiments were made with potassium nitrate, the affinities of the various hydrates for water being 1.74, 1.48, 1.48, 1.72 and 1.76 respectively.

T. H. P.

Inorganic Chemistry.

Alleged Conversion of Phosphorus into Arsenic. By ANASTASIOS K. CHRISTOMANOS (*Chem. Zeit.*, 1900, **24**, 943—944).—Arsenic trisulphide, prepared from commercial phosphorus by Fittica's method, was tested for phosphorus and nitrogen, but without success.

FRIEDRICH FITTICA replies that it is not surprising that the ordinary methods for the estimation of phosphorus and nitrogen should fail with arsenic, since the methods used for determining nitrogen in inorganic amino- or nitro-compounds are known to fail where the nitrogen is more firmly united, as in the case of many amino- and nitro-organic derivatives.

T. H. P.

Conversion of Phosphorus into Antimony. By FRIEDRICH FITTICA (*Chem. Zeit.*, 1900, **24**, 991—992).—The exact conditions are given under which, according to the author, phosphorus is oxidised to

arsenic and antimony by means of ammonium nitrate and carbonate, and potassium nitrite. The composition PN_2O is assigned to arsenic and $\text{P}_2\text{N}_2\text{O}_2$ to antimony. T. H. P.

Crystalline Form of Calcium, Barium, and Strontium Sulphides. By WILHELM MÜLLER (*Centr. Min.*, 1900, 178—179. Compare Abstr., 1898, ii, 376; 1899, ii, 97).—The material examined was prepared by E. Kunheim by heating in an electric furnace the sulphates of the alkaline earths with carbon: carbides are formed together with the sulphides. Cavities are lined with small cubes which are optically isotropic and have a perfect cubic cleavage. Sp. gr. (Kunheim): calcium sulphide, 2.4—2.5; strontium sulphide, 3.336. Mixed crystals of calcium and barium sulphide were also prepared. These sulphides are isomorphous with galena. L. J. S.

Cadmium Selenide. By HENRI FONZES-DIACON (*Compt. rend.*, 1900, 131, 895—897).—When cadmium chloride is heated just to its volatilising point in a current of hydrogen selenide, cadmium selenide, CaSe , is obtained in pale brown, transparent crystals of sp. gr. 5.81 at 15° , which, like the zinc selenide obtained under similar conditions (Abstr., 1900, ii, 345), seem to belong to the hexagonal system. A chocolate-brown selenide of the same composition is obtained by the action of hydrogen selenide or alkali selenides on solutions of cadmium salts. The yellow compound obtained by Fabre by the action of sodium selenide on a solution of cadmium iodide, is a double salt of the composition $\text{CdI}_2 \cdot 3\text{CdSe}$, which is decomposed by the action of light in the presence of water. The chloride and bromide form similar but less stable compounds. Cadmium selenide, even when crystallised, is easily decomposed by acids, burns readily when heated in oxygen, and is decomposed by chlorine at a moderate temperature.

C. H. B.

Thallium Chlorobromides. By VICTOR THOMAS (*Compt. rend.*, 1900, 131, 892—895. Compare Meyer, Abstr., 1900, ii, 655; Cushman, *ibid.*, 725).—Thallium chlorobromide, $\text{Tl}_3\text{Cl}_2\text{Br}_4$, is obtained by the action of excess of bromine on thallous chloride, and forms small, transparent, sulphur-yellow prisms which seem to be rhombic. They alter somewhat when exposed to air at the ordinary temperature and are decomposed by water, especially on heating. Oxy-acids liberate a large quantity of halogens; bromine converts the salt into a compound or compounds of the type Tl_2X_6 , whilst when heated it yields salts of the type Tl_2X_3 .

The action of varying quantities of bromine on thallous chloride also yields compounds of the types Tl_2X_3 and Tl_2X_6 , and these will be described subsequently. C. H. B.

Combination of Nitrogen with Metals of the Rare Earth Group. By CAMILLE MATIGNON (*Compt. rend.*, 1900, 131, 837—839. Compare Abstr., 1896, ii, 299; 1900, ii, 726).—Winkler has shown that metallic magnesium liberates the metal from the oxides of thorium, cerium, and lanthanum, and this is now found to be true for the oxides of praseodymium, neodymium and samarium. A mixture of the oxide of the metal and metallic magnesium was strongly heated in an

atmosphere of the gas to be investigated; it was found that nitrogen, but not argon, is rapidly absorbed by thorium, cerium, lanthanum, praseodymium, neodymium, and samarium.

The heat of formation of the oxides of thorium and cerium is greater than that of the oxides of the other metals, the oxide of samarium being the least exothermic.

H. R. LE S.

Direct Combination of Hydrogen with the Metals of the Rare Earths. By CAMILLE MATIGNON (*Compt. rend.*, 1900, 131, 891—892).—Neodymium, praseodymium, and samarium combine directly with hydrogen when the metals are liberated in the presence of this gas by the action of magnesium on the corresponding oxides. The hydrides thus formed are dissociated when strongly heated.

C. H. B.

Samarium Carbide. By HENRI MOISSAN (*Compt. rend.*, 1900, 131, 924—926).—*Samarium carbide*, SmC_2 , obtained by heating a compressed mixture of samarium oxide, Sm_2O_3 , with sugar carbon in the electric furnace, has a more metallic appearance than neodymium and praseodymium carbides (Abstr., 1900, ii, 726), but small particles are shown by the microscope to consist of transparent, yellow, hexagonal crystals; it has a sp. gr. 5.86. It is not reduced by hydrogen at 1000° , but is decomposed by chlorine when gently heated, and by bromine or iodine at a dull red heat. In oxygen at 400° , the carbide undergoes complete combustion, and it is also attacked by sulphur at a much higher temperature. In its action on water, samarium carbide resembles yttrium carbide, the gaseous products consisting of acetylene (71 per cent.), olefines (8 per cent.), and hydrogen and paraffins (21 per cent.). The carbide is readily decomposed by acids, and by hydrogen sulphide or hydrogen chloride at a red heat.

N. L.

Abrasive Efficiency of Corundum. By WILLIAM H. EMERSON (*Trans. Amer. Inst. Mining Engineers*, 1900, 29, 230—248).—Numerous comparative tests were made of the abrasive power of different samples of corundum from Georgia and North Carolina, and partial chemical analyses were made of the same material. There appears to be no close connection between abrasive power and chemical composition.

L. J. S.

Presence of Ferrous Oxythiocarbonate in the Water of the Rhone. By HENRI CAUSSE (*Compt. rend.*, 1900, 131, 947—949).—At certain periods during the last four years, it has been noticed that the water of the Rhone restores the colour of Schiff's reagent and exhibits other reactions characteristic of aldehydes. The reactions are first observed in June or July, reach a maximum in September, and disappear later in the year; they are not given by the water after distillation, or after exposure to air, which causes the formation of an ochreous deposit. Synthetic experiments show that the substance to which the reactions are due is probably ferrous oxythiocarbonate, $\text{CO} \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{Fe}$, formed by the combination of carbon dioxide with ferrous sulphide, the latter being the result of the reduction of sulphates by organic matter.

N. L.

Action of Steam and of Mixtures of Steam and Hydrogen on Molybdenum and its Oxides. By MARCEL GUICHARD (*Compt. rend.*, 1900, 131, 998—1001).—The brown molybdenum dioxide, MoO_2 , resulting from the action of hydrogen on the trioxide at 470° , is completely reduced by a current of the gas at 600° ; on the other hand, finely divided molybdenum is not oxidised by steam at temperatures below 700° . From these observations, it follows that the steam produced by the action of hydrogen on the oxides of molybdenum at 600 – 700° has no tendency to reverse the action, and may be considered as an inert gas; above 700° , however, it is a reagent and the inverse change becomes possible. When molybdenum and its dioxide are heated at these temperatures in a mixture of hydrogen and steam, both reactions, oxidation and reduction, occur simultaneously, and the state of equilibrium finally attained depends on the partial pressures of the constituents of the gaseous mixture. The metal or its dioxide is not affected at 800° by a current of the gaseous mixture containing its constituents in approximately molecular proportion; when the proportion of steam is larger than this, the metal is almost wholly oxidised to dioxide, whilst excess of hydrogen brings about a complete reduction of the oxide.
G. T. M.

Bismuth Phosphates. By CLEMENTE MONTEMARTINI and U. EGIDI (*Gazzetta*, 1900, 30, ii, 377—381).—The only phosphate obtainable from bismuth solutions by precipitation and subsequent washing is the ortho-phosphate, BiPO_4 , which is stable towards water even after boiling for some time, and is almost insoluble in sodium pyrophosphate solution.
T. H. P.

General Method of Separating the Metals that accompany Platinum. By ÉMILIE LEIDIE (*Compt. rend.*, 1900, 131, 888—891).—The residues from the manufacture of platinum and iridium are roasted in the air, heated in hydrogen, washed with dilute hydrochloric acid, again heated in hydrogen, and then mixed with sodium chloride and heated in chlorine at an incipient red heat. The residue and the volatilised products are treated with water, and the solution allowed to remain until the silver and the greater part of the lead and bismuth have separated as chlorides. The solution is heated at 100° and mixed gradually with excess of sodium nitrite, which precipitates the iron and gold, and afterwards with sodium carbonate, which precipitates lead, copper, bismuth, &c. After boiling for some time, the liquid is filtered, mixed with sodium hydroxide and distilled in a current of chlorine. The osmium and ruthenium are thus volatilised, and can be separated in the ordinary way. The residual liquid is acidified with hydrochloric acid, again mixed with excess of sodium nitrite, and a large quantity of ammonium chloride added, when the iridium and rhodium are precipitated as double ammonium nitrites. The precipitate is dissolved in hot hydrochloric acid, evaporated to dryness, dissolved in water and mixed with excess of ammonium chloride, which precipitates iridium, but not rhodium. The precipitate is dried and heated at 450° with its own weight of sodium chloride, which converts the iridium into soluble sodium iridochloride, and any co-precipitated rhodium into the insoluble anhydrous chloride.

The rhodium ammonium chloride is separated by crystallisation, dissolved in water, and converted first into the double sodium nitrite and afterwards into the double ammonium nitrite, which is precipitated, whilst any traces of iridium that may be present remain in solution.

The mother liquor from the iridium and rhodium contains platinum and palladium, and is evaporated to dryness, heated with concentrated hydrochloric acid to decompose the nitrites, again evaporated to dryness, and strongly heated. The residue is washed with water, dissolved in aqua regia, evaporated, redissolved and a current of nitric oxide passed into the liquid in order to reduce the palladium and iridium chlorides, after which the liquid is saturated with ammonium chloride to precipitate the platinum. The palladium in the mother liquor is precipitated by adding mercuric cyanide. C. H. B.

Mineralogical Chemistry.

Contributions to Chemistry and Mineralogy. By FRANK W. CLARKE (*Bull. U.S. Geol. Survey*, 1900, No. 167, 166 pp.).—This gives a collection of recently published researches which have been carried out in the laboratory of the United States Geological Survey by F. W. Clarke, W. F. Hillebrand, H. N. Stokes, G. Steiger, and N. H. Darton.

L. J. S.

Simultaneous Production of Two Nitrogen Compounds in the Crater of Vesuvius. By RAFF. VITT. MATTEUCCI (*Compt. rend.*, 1900, 131, 963—965).—The simultaneous ejection, during the recent eruption of Vesuvius, of fragments of rock coated, on the one hand, with ammonium chloride and, on the other, with iron nitride points to the existence of a genetic relation between these two substances. This view is in accordance with Silvestri's experiments.

ARMAND GAUTIER states that he has already referred to iron nitride as one of the sources of ammonium salts in volcanic lavas (this vol., ii, 14).

N. L.

Separation of Titaniferous Iron-Ores in Basic Igneous Rocks. By JOHAN H. L. VOGT (*Chem. Centr.*, 1900, ii, 818—819; from *Zeit. prakt. Geol.*, 1900, 233—242).—Previous papers by the author have treated in detail the concentration (magmatic differentiation) of ores of iron, nickel, &c., in igneous magmas. A description is now given of two types of separation, namely, of titaniferous iron-ore and of magnesium silicate, from the same magma at Lofoten in northern Norway. Analysis of spinel (pleonaste) from a basic separation at Solnör, Norway, gave :

| Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | MgO. | Total. |
|----------------------------------|----------------------------------|------|------|-------|--------|
| 61·8 | 4·6 | 18·1 | 1·05 | 14·75 | 100·3. |

L. J. S.

Chromite from North Carolina. By JOSEPH HYDE PRATT (*Trans. Amer. Inst. Mining Engineers*, 1900, 29, 17—39).—This covers the same ground as a previous paper (Abstr., 1899, ii, 494). The following additional analysis by C. Baskerville is given of chromite from Burnsville, Yancey Co.:

| Cr ₂ O ₃ . | Al ₂ O ₃ . | FeO. | MgO. | SiO ₂ . | CaO. |
|----------------------------------|----------------------------------|-------|------|--------------------|-------|
| 58.00 | 15.52 | 14.45 | 8.26 | 3.20 | 0.70. |

L. J. S.

Blödite from Hallstatt. By RUDOLF KOEHLIN (*Ann. naturhist. Hofmus. Wien*, 1900, 15, 103—110).—A crystallographic description is given of a new find of blödite ("simonyite") from Hallstatt. Some of the crystals have a dull, weathered surface, but those in freshly-opened cavities are bright. As "simonyite" from Hallstatt was supposed to differ from blödite in not efflorescing in the air, the following analysis by Ernst Brezina has been made of the dull crystals:

| SO ₃ . | MgO. | Na ₂ O. | H ₂ O. | Total. |
|-------------------|-------|--------------------|-------------------|--------|
| 47.45 | 12.16 | 19.79 | 20.99 | 100.39 |

This gives the blödite formula, $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$. At 108°, there is a loss of 8.51 per cent., and at 200° all the water is expelled. Associated with the blödite are polyhalite, anhydrite, salt, gypsum, and glauberite. A crystallographic description is given of the glauberite.

L. J. S.

Ceruleite, a New Mineral. By HENRI DUFET (*Bull. Soc. franç. Min.*, 1900, 23, 147—150).—This occurs as turquoise-blue, clay-like masses in the Emma Luisa Mine at Huanaco, Taltal, Chili. Sp. gr., 2.803. Under the microscope, it is seen to be minutely crystalline. Analysis I gives the formula $\text{CuO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{As}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$. At 180°, there is a loss of only 1.45 per cent.

| | As ₂ O ₅ . | Al ₂ O ₃ . | CuO. | H ₂ O. | SiO ₂ . | Total. |
|-----|----------------------------------|----------------------------------|-------|-------------------|--------------------|--------|
| I. | 34.56 | 31.26 | 11.80 | 22.32 | — | 99.94 |
| II. | 1.8 | 38.8 | trace | 19.1 | 40.6 | 100.3 |

Associated with the ceruleite is a white clay resembling halloysite, which on analysis gave the results under II. Both minerals contain minute scales of gold, 1 per cent. of which has been deducted from analysis II.

L. J. S.

Cordierite from Celebes and Germany. By HUGO BÜCKING (*Ber. Senckenb. Ges. Frankfurt. a. M.*, 1900, 20 pp.).—Among the ejected blocks of andesite from the volcano Seputan in north Celebes are a few shining black fragments which resemble obsidian in appearance. Thin sections under the microscope, however, show that this material consists almost wholly of minute fresh crystals of cordierite, with very little glass, iron-ore (about 4 per cent.) and either augite or sillimanite. The following bulk analysis by W. Bruhns of the material shows that, although the results are in approximate agreement with the formula of cordierite, most of the magnesium of normal cordierite is replaced by calcium and iron.

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | CaO. | MgO. | Loss on ignition. | Total. | Sp. gr. |
|--------------------|----------------------------------|----------------------------------|-------|------|------|----------------------|--------|---------|
| 49·15 | 31·84 | 2·88 | 11·49 | 4·30 | 0·55 | 0·06 | 100·27 | 2·65 |

A description is also given of the cordierite which occurs in the altered ("vitrified") sandstones in contact with basalt in central Germany.
L. J. S.

Crystallographic Constants and Chemical Composition of Tourmaline. By ERNST ANTON WULFING (*Programm z. 82 Jahresfeier d. k. Württemb. landwirt. Akad. Hohenheim*, 1900, 99 pp. Compare Abstr., 1889, 765; 1900, ii, 602).—Previously published constants are discussed, and numerous new crystallographic, optical and density determinations are given of material which was, whenever possible, the same as that analysed by previous authors. For crystals from various localities the angle γ varies from $46^{\circ}48'$ to $47^{\circ}15'$, the corresponding values of the c axis being 0·4469 and 0·4521 respectively. The refractive indices and double refraction also vary considerably: $\epsilon = 1·6159$ to $1·6572$; $\omega = 1·6354$ to $1·6918$ (for line E). Sp. gr. $3·007$ to $3·240$. The double refraction and the sp. gr. both increase with the amount of iron. Four groups of tourmaline may be distinguished, namely, those rich in lithium, ferrous iron, ferric iron or magnesium; the iron tourmalines are black, but those of the second group have pale reddish-violet and blue as axial pleochroism colours, whilst those of the third group have brownish and dark green. The variations in the chemical composition of tourmaline are well illustrated by a coloured plate giving graphically the results of 33 of the best analyses.
L. J. S.

New Mineral Occurrences [Inesite] By OLIVER CUMMINGS FARRINGTON (*Field Columbian Museum, Chicago, Geol. Series*, 1900, 1, 221—231).—The rare mineral inesite has been found at San Cayetano mine, near Villa Corona, State of Durango, Mexico, where it occurs as radiating tufts of flesh-red crystals. Measurements and figures are given of the crystals, and an analysis gave the results under I. At 110° there is a loss of 3·88 and at 240° of 1·94 per cent., the rest of the water being given off at a red heat; the formula is therefore written as $H_2(Mn,Ca,Fe)_6Si_6O_{19} + 3H_2O$.

| | SiO ₂ . | MnO. | FeO. | CaO. | MgO. | H ₂ O. | Total. | Sp. gr. |
|-----|--------------------|-------|------|-------|-------|-------------------|--------|---------|
| I. | 44·89 | 36·53 | 2·48 | 8·24 | trace | 8·20 | 100·34 | 2·965 |
| II. | | | 1·18 | 28·27 | 22·46 | | | 2·878 |

A compact white dolomite from near Lakeport, Lake Co., California, gave the results under II; it is used by the Indians as money. Crystallographic descriptions are also given of caledonite, gaylussite, epsomite and calcite from new localities in the United States.

L. J. S.

Granite Rocks of Butte, Montana [Analyses of Biotite and Hornblende]. By WALTER HARVEY WEED (*J. Geol.*, 1899, 7, 737—750).—In a petrographical paper on the granite and associated rocks in the neighbourhood of Butte, the following mineral analyses,

by H. N. Stokes, are given: I, black biotite; II,* very dark-green hornblende, with a large angle of optical extinction; both minerals were isolated from the Butte granite, of which the average composition is given under III:

| | SiO ₂ . | TiO ₂ . | P ₂ O ₅ . | F. | Cl. | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | BaO. |
|-------|--------------------|--------------------|---------------------------------|------|------|----------------------------------|----------------------------------|-------|------|------|
| I. | 35.79 | 3.51 | 0.10 | 0.76 | 0.20 | 13.70 | 5.22 | 13.72 | 0.19 | 0.13 |
| II. | 45.73 | 1.43 | 0.35 | 0.28 | — | 6.77 | 4.94 | 10.39 | 0.54 | nil |
| [III. | 64.03 | 0.60 | 0.18 | — | — | 15.58 | 1.96 | 2.83 | 0.11 | 0.07 |

| | SrO. | CaO. | MgO. | K ₂ O. | Na ₂ O. | Li ₂ O. | H ₂ O below 110°. | H ₂ O above 110°. | Total, less O for F. & Cl. |
|------|------|-------|-------|-------------------|--------------------|--------------------|------------------------------------|------------------------------------|----------------------------------|
| I. | nil | 0.05 | 12.13 | 9.09 | 0.15 | trace | 1.21 | 3.64 | 99.22 |
| II. | nil | 11.25 | 12.32 | 1.22 | 0.77 | trace | 0.49 | 2.29 | 98.65 |
| III. | 0.04 | 4.20 | 2.15 | 4.11 | 2.76 | — | 0.20 | 0.73 | 99.87 |

L. J. S.

Analyses of Rocks. By FRANK W. CLARKE (*Bull. U.S. Geol. Survey*, 1900, No. 168, 308 pp.).—This is a new and enlarged edition of the second portion of *Bulletin* No. 148 (1897). It gives a collection of 1404 detailed analyses of rocks (including igneous and crystalline rocks, sandstones, carbonate-rocks, slates and shales, clays, soils, &c.) and meteorites, and of minerals isolated from them, which have been made during the years 1880—1899 in the laboratory of the United States Geological Survey.

L. J. S.

Meteorite from Lançon, France. By STANISLAS MEUNIER, (*Compt. rend.*, 1900, 131, 969—972).—This stone was seen to fall on June 20, 1897, at Lançon, Dept. Bouches-du-Rhône. Besides the usual black crust, there are internal black surfaces which are seen on fractures as fine "cosmic lines." From a partial mechanical and chemical analysis, the mineralogical composition is deduced as: nickel-iron 8.80; pyrrhotite, 6.35; chromite, 0.54; enstatite, and plagioclase, 52.21; olivine, [32.10]=100.00. Sp. gr. 3.482. The nickel-iron contains 8.21 per cent. of nickel. Thin sections under the microscope show an intimate mixture of crystalline fragments.

L. J. S.

Water from the Kiedrich Spring near Eltville, Rhine. By HEINRICH FRESSENIUS (*Jahrb. Nassau. Ver. Naturk.*, 1900, 53, 1—21).—Water from this saline spring in the Kiedrichthal issues at a temperature of 24.3°, and has sp. gr. 1.006630 at 17.5°. It has a salty taste and is clear and colourless, but becomes cloudy on standing. The analytical results are compared with an analysis of the same water made by C. Bischoff in 1888, and with analyses of waters from several other salt springs.

L. J. S.

* In anal. II are inserted corrections made by the author; compare *Bull. U. S. Geol. Survey*, 1900, No. 168, 116.

Physiological Chemistry.

Peptic Digestion. By HANS MALFATTI (*Zeit. physiol. Chem.*, 1900, 31, 43—48).—The prolonged action of pepsin-hydrochloric acid on Witte's peptone leads to the formation of tryptophan. Leucine, tyrosine, and hexon bases were found in small quantities in some cases. These products are generally regarded as characteristic of tryptic digestion, and the question is discussed whether they are produced by the activity of pepsin itself, or of another ferment which contaminates the pepsin. The former explanation is regarded as more probable, although it is weakened by the discovery that all preparations of pepsin, some of which may be intensely active, do not cause the appearance of the products named. Attempts to separate a second ferment failed.

W. D. H.

The Rennet and Anti-Rennet-like Action of Blood. By E. FULD and KARL SPIRO (*Zeit. physiol. Chem.*, 1900, 31, 132—155).—The rennet-like action of blood is not due to serum-albumin, but to that portion of the globulin which is precipitable by dialysis (euglobulin); the anti-rennet action is associated with the portion of the serum-globulin which is not precipitable by dialysis (pseudo-globulin); this action is probably associated with its affinity for calcium.

W. D. H.

Cryoscopy of the Human Sweat. By P. ARDIN-DELTEIL (*Compt. rend.*, 1900, 131, 844—845).—From determinations of the freezing point of 14 samples of healthy human sweat, the following conclusions are drawn: (1), the mean freezing point is -0.237° ; (2), this varies with different individuals between -0.08° and -0.46° ; (3), the variations depend, for the greater part, on the amount of sodium chloride in the sweat. The lowest values observed were obtained during the summer.

H. R. LE S.

Creatinine. By ADALBERT GREGOR (*Zeit. physiol. Chem.*, 1900, 31, 98—118).—Experiments were made on the reducing power of creatinine; the numbers obtained closely approximate to those of G. S. Johnson. Salkowski's method is regarded as the most accurate for quantitative purposes. Beer drinking was found to increase the reducing properties of urine, but this is not due to variations in creatinine. Muscular exercise produces a marked increase in the urinary creatinine, and creatinine is regarded as a specific product of muscular metabolism.

W. D. H.

Diuretic Action of Isotonic Salt Solutions. By R. MAGNUS (*Chem. Centr.*, ii, 1900, 1031; from *Arch. exp. Path. Pharm.*, 44, 396—433).—Isotonic solutions of sodium chloride and sodium sulphate produce equal dilution of the blood, but the latter is a more powerful diuretic, because of its direct action on the kidneys. Three kinds of diuresis are described: (1), water diuresis dependent on increase of water in the blood; (2), salt diuresis, as in that produced by Glauber's

salts ; and (3), combined salt and water diuresis in which both factors are concerned. W. D. H.

Pathology of Diabetic Coma. By KARL GRUBE (*Chem. Centr.*, ii, 1900, 1030—1031 ; from *Arch. exp. Path. Pharm.*, 44, 349—362).—Sternberg states (*Zeit. klin. Med.*, 38, 65) that β -aminobutyric acid is the toxic material in diabetic coma, this passing into the urine as β -hydroxybutyric acid. Injection of the amino-acid in cats produces coma ; the urine gives Fehling's, Gerhard's, and Lieben's reactions, and contains acetone. W. D. H.

Metabolism in Gout. By CHALMERS WATSON (*J. Pathol. and Bacteriol.*, 1900, 7, 103—117).—A large number of observations are recorded, both as regards the blood, uric acid, and the influence of nucleic acid. The results suggest that in gout the formation of uric acid from the metabolism of the absorbed nucleins and its excretion are altered in no important way from the normal state. The primary changes in gout must probably be looked for in general intracellular metabolism. W. D. H.

The Activity of Saliva in various Diseased Conditions. By W. G. AITCHISON ROBERTSON (*J. Pathol. and Bacteriol.*, 1900, 7, 118—128).—Attention is directed to the importance of examining the amount and activity of the saliva in disease. Numerous observations are recorded here both in children and adults. The practical importance of the question is seen in dieting ; starchy foods should naturally be withheld, or if given should be previously diastased, in cases where the secretion is scanty or in abeyance, as in fever, and the acute infectious diseases ; in dilatation of the stomach, the saliva contains almost no ptyalin ; morphine and atropine inhibit the secretion. W. D. H.

An Albumose in Urine. By J. A. MILROY (*J. Pathol. and Bacteriol.*, 1900, 7, 95—102).—An account is given of the properties of an albumose occurring in the urine of a patient who probably suffered from bone disease. The characters of the albumose do not agree fully with those of any substance previously described, although they approach nearest to those of deutero-albumose. W. D. H.

Interesting Abnormal Urines. By RUDOLF KOBERT (*Chem. Centr.*, 1900, ii, 919—920 ; from *S. Korresp. Bl. Allgem. Mecklenburg. Aerzte-Ver.*, 1900, No. 212).—Cases of cystinuria, indicanuria and diaceturia are described. These are somewhat rare conditions, but nothing new appears to have been made out. W. D. H.

Poisonous Effects of Saline Solutions. By ANNE MOORE (*Amer. J. Physiol.*, 1900, 4, 386—396).—The facts described by Loeb regarding the poisonous effects of pure sodium chloride solutions on marine organisms are also true for fresh-water animals (young trout and tadpoles). The chlorides of calcium, potassium, magnesium, and lithium are also poisonous. The poisonous effects of sodium chloride may be antagonised by calcium. W. D. H.

A Volatile Venom from the Skin of *Iulus Terrestris*. By C. PHISALIX (*Compt. rend.*, 1900, 131, 955—957).—The cutaneous secretion of the myriapod *Iulus terrestris* has a yellow colour, and when injected intraperitoneally in guinea pigs proves fatal. The autopsy shows extensive peritonitis. The active material in this venom is not proteid but some volatile substance. W. D H.

Quinone as the Active Principle of the Venom of *Iulus Terrestris*. By AUGUSTE BÉHAL and C. PHISALIX (*Compt. rend.*, 1900, 131, 1004—1007).—The aqueous solution of the venom of *Iulus terrestris* has a yellow colour and contains a quinonoid substance which, in all probability, is benzoquinone. G. T. M.

Chemistry of Vegetable Physiology and Agriculture.

A Possible Cause of Clumping in Bacilli. By SIR THOMAS LAUDER BRUNTON (*J. Pathol. and Bacteriol.*, 1900, 7, 53—54).—Wooden matches covered with hard soap to imitate bacteria remain separate in neutral or alkaline water, but if the water is acidified they clump together. The same is true for the formation of rouleaux in cork models of red blood corpuscles. It is suggested that the formation of clumps and rouleaux respectively is due to some slight alteration of their surfaces produced by the liberation of some fatty substance by means of carbon dioxide. W. D. H.

A Proteolytic and Rennet-like Ferment in Malt. By FR. WEIS (*Zeit. physiol. Chem.*, 1900, 31, 79—97).—In the green and dry malt, there is present both a proteolytic (peptase) ferment and one which curdles milk. Most attention is directed to the latter; this acts best in an acid (especially lactic acid) medium, and plays an important part, not only in the germinating process in the plant, but also in the making of beer. W. D. H.

Presence of Seminase in Non-germinating Seeds containing Horny Albumen. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1900, 131, 903—905).—The non-germinating seeds of *Medicago sativa* and *Indigofera tinctoria* contain a small quantity of seminase which can be extracted from the finely ground seeds by treatment with water. Like the seminase produced during germination (*Abstr.*, 1900, ii, 233), it converts the horny albumen of the seeds into assimilable sugars. C. H. B.

Exosmosis of Diastase by young Seedlings. By JULES LAURENT (*Compt. rend.*, 1900, 131, 848—851).—The germinating seeds of maize, wheat, peas, and buckwheat are able to furnish a part of the diastase necessary for the digestion of their reserve food material, and are thus able to assimilate insoluble organic substances such as starch. This phenomenon ceases at the end of the germinating period. Experiments carried out by a method previously described (*Compt. rend.*,

1897, 125, 887) clearly show that the roots are incapable of exuding any appreciable quantity of amylase.

H. R. LE S.

Assimilation in two Cultivated Plants. By ALEXIUS VON SIGMOND (*Chem. Centr.*, 1900, ii, 1087; from *J. Landw.*, 48, 251—264).—Maize plants develop slowly during the first period of growth, but more quickly from this time to the flowering period. Growth is then checked for a time, but afterwards quickens. During the deposition of starch, the growth is again checked, after which, during the ripening of the grain, assimilation becomes very vigorous. On the whole, assimilation and development go together, and no special manure seems to be necessary.

In the case of tobacco, development was slow in the early stages of growth, and increased and diminished alternately during the subsequent periods. There seems to be a slight temporary want of phosphoric acid in the first period, and also of nitrogen; the importance of nitrogen increases before the beginning of the first period of greater activity. These results accord with what has been observed in practice.

N. H. J. M.

Angostura Barks. By C. HARTWICH and M. GAMPER (*Arch. Pharm.*, 1900, 238, 568—587).—The interest of the paper is chiefly pharmaceutical, and that in the botanical direction. The bark of *Esenbeckia febrifuga* (*syn. Evodia febrifuga*), sold under the name of angostura bark, was examined chemically; from it, 0.11 per cent. of a solid "ethereal oil" melting at 37—42° was obtained by distillation with steam; and by percolation with 1 per cent. aqueous tartaric acid, 3.9 per cent. of alkaloids was obtained. From this mixture, five alkaloids were separated by taking advantage of the differences in the ease with which they are liberated by ammonia and by sodium hydroxide, and by the differences in their solubility in ether, chloroform, and absolute alcohol.

C. F. B.

Hibiscus Esculentus. By ALEXANDER ZEGA (*Chem. Zeit.*, 1900, 24, 871).—The green fruit of *Hibiscus esculentus*, which is sold in Servia as a vegetable under the name of 'Bamnje,' has the following mean percentage composition: water, 80.74; nitrogenous material, 4.15; fat, 0.42; carbohydrates, 12.12; wood fibre, 1.15; ash, 1.41, the percentages of nitrogenous material and carbohydrates on the dry material being 21.55 and 63.24 respectively. The ash contains SiO₂, 0.06; SO₃, 0.034; phosphoric acid, 0.043; CaO, 0.100; MgO, 0.016; K₂O, 0.042; Na₂O, 0.058 per cent. of the original substance.

T. H. P.

"Radix Naregamiae." By RUDOLPH HAUKE (*Chem. Centr.*, 1900 ii, 1129—1130; from *Zeit. Oesterr. Apoth.-Verein.*, 38, 829—833).—An ethereal extract of "*Radix Naregamiae*" contained 0.3 per cent. of Hooper's alkaloid naregamine, 2.0 of wax, 2.5 of resin, and 0.9 of fatty oil and colouring matter. The wax melted at 58°, had a sp. gr. 0.91, acid number 5.9 (chloroform solution), 6.1 (alcoholic solution), ether number 21.1, and saponification number 27.0. When the alcoholic solution was poured into water, a resin was precipitated, whilst in the solution there still remained a substance which readily

reduced Fehling's solution (sugar). The aqueous extract had a faint acid reaction and gave a blue coloration with iodine; a crystalline compound, which is probably asparagine (Hooper), was also isolated and the extract contained proteids, gum, and pectin substances but not tannin. The drug left 5.73—7.1 per cent. of ash, that of the wood being 1.79 and that of the bark 5.97; 5.9 per cent. of dry residue was obtained from the alcoholic and 12.3 from the aqueous extract.

E. W. W.

Simarubaceæ I. Samadera Indic. By J. L. B. VAN DER MARCK (*Chem. Centr.*, 1900, ii, 1124—1125; from *Ned. Tijds. Pharm.*, 12, 296—306).—The seeds of *Samadera Indic.* contain 63 per cent. of fat, which consists of 87.7 per cent. of triolein, 8.41 of tripalmitin, and 3.89 of tristearin. The alcoholic extract contains an alkaloid which appears to be identical with gliadine and a resin; glucosides and a bitter principle are present in the seeds. The bitter principle is also contained in the bast and is accompanied by tannic acid; it is somewhat soluble in alcohol and acetone, melts at 255°, and is apparently identical with Rost van Tonningen's samaderin. It contains carboxyl groups but neither a methoxy- nor an ethoxy-group, and when administered to cold blooded animals causes paralysis of the voluntary nerves and death.

A second bitter principle is found in the roots; it melts at 209°, is soluble in alcohol and sodium hydroxide solution, and is apparently identical with quassin.

E. W. W.

[Feeding Experiments with Cows.] By EBERHARD RAMM (*Bied. Centr.*, 1900, 29, 737; from *Milch-Zeit.*, 1899, 52, 817. Compare Abstr., 1900, ii, 749).—A summary of the results of experiments already described. Besides the actual results, corrected results are given, excluding the effects of period of lactation, on the assumption that the same food produces the same effect. The conclusion is drawn that when rich foods are employed, it is undesirable to go beyond a certain limit as regards the amounts of proteid and fat in the rations. Certain foods exert a specific action which does not depend on the amounts of nutritive substances they contain.

N. H. J. M.

Value of Molasses-Foods. By MAX GONNERMANN (*Chem. Centr.*, 1900, ii, 1034; from *Milch-Zeit.*, 29, 599).—Oil seeds mixed with molasses may undergo considerable loss when long kept, and mixtures of brewer's grains with molasses, if not quite dry, may decompose rapidly, owing to the presence of yeasts and bacteria. Under these conditions, all the sugar and nitrogenous substances may be lost, and injurious compounds may be produced. The employment of peat-meal molasses is strongly recommended; it may be mixed with oil-seeds as required.

N. H. J. M.

Nutritive Value of Orange Residues in Calabria. By FAUSTO GABRIELLI (*Bied. Centr.*, 1900, 29, 780; from *Staz. sper. agrar. ital.*, 1899, 32, 204).—The residues of oranges, &c., in Calabria are utilised as cattle food, especially after being allowed to decompose until they acquire a uniform buttery consistence. The following are the results of analyses of (1) lemon, (2) Bergamot orange, residues, and (3) the mixed

residues, fermented; water in fresh substance (1) 89.10, (2) 88.53, (3) 92.91 per cent. Percentage composition of the dry matter:

| | Total N. | Proteid N. | Fat. | Non- nitrogenous extract. | Crude fibre. | Ash. | K ₂ O. | P ₂ O ₅ . |
|----|-------------|---------------|------|---------------------------------|-----------------|------|-------------------|---------------------------------|
| 1. | 0.60 | 0.36 | 0.97 | 80.39 | 12.03 | 4.34 | 0.53 | 0.36 |
| 2. | 0.65 | 0.44 | 1.09 | 82.21 | 9.20 | 4.75 | — | 0.29 |
| 3. | 1.38 | 0.78 | 5.51 | 61.33 | 21.80 | 6.52 | 1.36 | 0.38 |

Milk and meat from animals fed with the residues have a characteristic, but not unpleasant, taste. N. H. J. M.

Relation between the Weight and the Percentage of Nitrogen in Wheat Grain. By WILHELM JOHANNSEN and FR. WEIS (*Bied. Centr.*, 1900, 29, 758—760; from *Tidsskr. Landw. Planteavl.*, 1899, 5, 91—99).—The results of analyses of large, average, and small grains of different varieties of wheat show that, as in the case of barley (Abstr., 1900, ii, 363), a relation exists between the weight and the percentage of nitrogen, which is highest in the large grains. There are, however, many exceptions, and the rule cannot be adopted for improving varieties of wheat and barley. The large, mealy grains, which were always heavier than the average of the whole, invariably contained less nitrogen than the whole sample. N. H. J. M.

Manurial Experiments with Hops. By MAX BARTH (*Bied. Centr.*, 1900, 29, 728—731; from *Bl. Gersten-, Hopfen-, u. Kartoffelbau.*, 1899, 323).—The results of field experiments showed that hops require mineral manures as well as nitrogen even on fertile soils. N. H. J. M.

Green Manure Experiments with Potatoes. By CLAUSEN (*Bied. Centr.*, 1900, 29, 733—735; from *Illust. Landw. Zeit.*, 1900, 129).—The average yield of potatoes, with various manures, after lupins as green manure, was 135, taking the yield of the potatoes without green manure as 100. The results of experiments with different varieties of potatoes showed that those varieties with the longer vegetative periods seem to benefit less than those with short vegetative periods.

Both kainite and superphosphate, with green manure, further increased the yield of potatoes. N. H. J. M.

Effect of Water and Manure on the Composition of Potato Ash. By A. VON DASZEWSKI (*Chem. Centr.*, 1900, ii, 1086—1087; from *Inaug.-Diss. Göttingen*, 1900).—An extension of the work commenced by Wilms (Abstr., 1900, 164). With excessive moisture, the assimilation of potassium and phosphoric acid is absolutely greater and relatively less than with less moisture, whilst relatively greater amounts of calcium and chlorine are taken up.

The application of a substance as manure causes an increased amount of the substance to be taken up by the plant, especially by the leaves. Calcium and chlorine have the predominating action in decreasing the starch in presence of much moisture.

In preparing the ashes, Tucker's apparatus was employed, and it was found that the method rendered incineration more easy and checked

volatilisation (Abstr., 1900, ii, 52; Shuttleworth and Tollens, *ibid.*, 111; and Shuttleworth, *ibid.*, 372).
N. H. J. M.

Alkali Soils of the Yellowstone Valley. By MILTON WHITNEY and THOMAS H. MEANS (*U.S. Dept. Agr. Div. of Soils, Bull.*, 1898, 14, pp. 39).—The ultimate source of the alkali is the sandstone. Before irrigation was introduced, the salts were well distributed throughout the soil, which then contained rather large, but not injurious, amounts of alkali.

To get rid of the excess of alkali where it has become localised, a system of drainage will have to be adopted, whilst great care must be exercised in irrigation. In this manner, the original fertility of the soil may be restored in a few years.
N. H. J. M.

Movement of Water and Solutions of Salts in Soil. By S. KRAWKOW (*Chem. Centr.*, 1900, ii, 1084—1085; from *J. Landw.*, 48, 209—222).—The movement of water is much slower in loamy sand than in diluvial sand. The rate and height of capillary movement is in inverse ratio to the amount of moisture. The amount of drainage and the rate are directly proportional to the amount of rain.

In the case of solutions of salts, the rate of upward capillary movement depends on the degree of concentration and not on the nature of the salt. Application of gypsum and calcium carbonate increased the rate of drainage as well as that of the upward capillary movement.

N. H. J. M.

Analytical Chemistry.

Estimation of Nitrites Alone or in the Presence of Nitrates. By HENRI PELLET (*Chem. Centr.*, 1900, ii, 1089; from *Ann. Chim. anal. appl.*, 1900, 5, 361—365).—The author republishes a process given by him in 1879, and based on the fact that in the presence of ferrous salts and hydrochloric acid both nitrates and nitrites yield nitric oxide, but that when acetic acid is substituted for hydrochloric acid only the nitrites are decomposed. L. DE K.

Estimation of Nitrites and their Separation from Nitrates. By LUCIEN L. DE KONINCK (*Chem. Centr.*, 1900, ii, 1089—1090; from *Ann. Chim. anal. appl.*, 1900, 5, 365—368).—The method proposed by Pellet (preceding abstract) is approved of. A large excess of hydrochloric acid is essential for the reaction when dealing with nitrates. Nitrites are completely decomposed by boiling with ferrous ammonium sulphate alone. In the presence of ammonium chloride, free nitrogen is evolved, but this makes no difference, as the volume of gas evolved is the same. L. DE K.

Estimation of Arsenic. By O. DUCRU (*Compt. rend.*, 1900, 131, 886—888).—The arsenic is precipitated as ammoniacal cobalt arsenate (this vol., ii, 23), the reagents required being a solution of 75 grams of

cobalt chloride in 1000 c.c. of water and a solution of ammonium acetate prepared by neutralising a 40 per cent. solution of glacial acetic acid with a 20 per cent. solution of ammonia. The arsenic solution is concentrated, acidified if necessary with hydrochloric acid to decompose any alkali carbonates, and then just neutralised with ammonia. Ten c.c. of the cobalt solution for every 100 mgrms. of arsenic present are mixed with one-quarter its volume of the ammonium acetate solution, and to the mixture is added about 3 per cent. of a 20 per cent. solution of ammonia. This reagent and the arsenic solution are mixed and heated in a closed flask on a water-bath until the precipitate becomes crystalline; it is then collected and washed with cold water. The precipitate may be dried at 100° and weighed, when it has the composition $\text{Co}_3(\text{AsO}_4)_2, \text{NH}_3, 7\text{H}_2\text{O}$, or it may be heated at dull redness until the weight is constant, which does not yield very good results; or it may be dissolved in dilute acid, the arsenic separated and the cobalt precipitated by electrolysis in presence of ammonium sulphate. The method yields accurate results even with very small quantities of arsenic. C. H. B.

An Improvement on the Geissler Potash Apparatus. By J. WETZEL (*Ber.*, 1900, 33, 3393—3394).—To insure the complete absorption of carbon dioxide in combustions, where the gas is given off very rapidly, the author proposes the addition of a small moveable inverted funnel in each of the three bulbs, which contain the potash of the usual Geissler apparatus. R. H. P.

Estimation of Carbon in Ferrochrome. By ANDREW A. BLAIR (*J. Amer. Chem. Soc.*, 1900, 22, 719—723).—Twenty-five grams of pure potassium hydrogen sulphate are placed in a platinum boat 150 mm. long and 25 mm. wide and fused over a bunsen burner to destroy any carbonaceous matter. When cold, 1 gram of the finely powdered sample is sprinkled over it, and the boat is inserted into a larger one, which is then fitted with a cover so arranged that any particles spirted up from the melting mass run into the larger boat; by this means, the combustion tube is kept clean.

The latter consists of a platinum tube 400 mm. long and 30 mm. in diameter closed with a ground joint at the rear. The forward end for a distance of 75 mm. is contracted to 12 mm. and filled with platinumised asbestos. It is then further contracted to 6 mm. in diameter and a piece of glass tube filled with glass beads is fused to it after being bent downwards at an angle of 90° . The plugs are made of pumice wrapped with platinum foil and are pushed in after the boat.

It will be noticed that the use of india-rubber stoppers is entirely avoided, which is very essential, as these may be a source of considerable error.

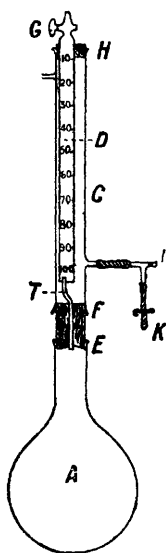
The further details of the process are briefly as follows. The combustion is made in a slow current of purified oxygen, the bulk of the liberated sulphuric acid condenses in the tube containing the beads, and the gases are then passed through two glass flasks kept hot and containing a solution of chromic acid in sulphuric acid to retain any sulphur dioxide. After passing over pumice stone saturated with chromic acid and over dry calcium chloride, the carbon dioxide is

finally absorbed in the usual manner and weighed. The guard tube of the absorption apparatus is connected with a gasometer which acts as an aspirator and relieves the pressure in the apparatus, which otherwise might become excessive owing to the condensation of sulphuric acid in the bent tube. L. DE K.

Some Principles and Methods of Rock Analysis. By WILLIAM F. HILLEBRAND (*Bull. U.S. Geol. Survey*, 1900, No. 176, 114 pp.).—This, which is a new and enlarged edition of the first portion of *Bulletin* No. 148 (1897), gives detailed descriptions of the methods employed in the laboratory of the United States Geological Survey for the analysis of silicate rocks and minerals. Several diagrams of apparatus are given, and also a complete index. L. J. S.

Separation of Tungsten Trioxide from Molybdenum Trioxide. By MAX J. RUEGENBERG and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1900, 22, 772—773).—The two oxides may be quantitatively separated by heating them with about 50 times their weight of sulphuric acid of sp. gr. 1.378, which completely dissolves the molybdenum trioxide but leaves the tungsten trioxide undissolved. The presence of even a large excess of ferric oxide does not interfere with the estimation of the tungsten. L. DE K.

Estimation of Air in Water. By HENRI PELLET (*Chem. Centr.* 1900, ii, 1088—1089; from *Ann. Chim. anal. appl.*, 1900, 5, 369—370).—*A* (see Fig.) is a glass flask, *E* an india-rubber cork with a glass tube *T*, *C* a condenser the cork, *F*, of which rests on *E*. *D* is a graduated tube closed by the stopcock, *G*, and supported by *H*. *I*, *J*, and *K* serve for regulating the refrigerating water.



A is filled with the sample to be tested, the cooling water is admitted into *C*, the burette, *D*, is filled with water by applying suction and connected with *T*. On warming *A*, a portion of the water is expelled, the same volume which flows from *J*, is measured and deducted from the volume of the balloon, *A*. The air from the water collects in *D*, and its volume is measured with due regard to temperature and pressure. The gas may be removed by opening *G*, and further examined.

L. DE K.

Preliminary Operations at the Spring for the Detection of Metals Present in Minute Quantities in Natural Waters.

By F. GARRIGOU (*Compt. rend.*, 1900, 131, 897—899).—In order to avoid the evaporation of large quantities of water, the author collects the water at its source in large vessels of glass or wood, adds excess of barium hydroxide in very fine powder, and agitates briskly. After the precipitate has completely

settled, the clear liquid is drawn off and the precipitate collected in flasks. The liquid is mixed with a slight excess of sulphuric acid, and the precipitate, which carries down with it traces of metals not precipitated by the hydroxide, is also collected. The two precipitates contain all the metals originally present in the water, with the exception of alkali metals.

C. H. B.

Quantitative Reactions to distinguish between Petroleum or Cannel Coal Pitches and Pitches from Distillation of Fats. By D. HOLDE and J. MARCUSSEN (*Ber.*, 1900, 33, 3171—3175).—Soft pitches from fat distillation, stearin pitch, wool pitch, &c., are readily distinguished from the soft and hard pitches from petroleum by means of the large amounts of fatty acids and esters contained in them. Hard wool and stearin pitches are somewhat difficult to differentiate from petroleum pitches, as they contain only small amounts of acids. The distillates from such pitches yield 14—17 per cent. of snow-white paraffin hydrocarbons; the sp. gr. of the distillate is always considerably below 1, as are the sp. grs. of the distillates from petroleum or cannel coal pitches. Coal tar pitch, on the other hand, yields distillates of sp. grs. always above 1.

The best method of distinguishing hard fatty and "mineral oil" pitches is by the aid of a specially prepared alcoholic-ether extract. The extract from hard fatty pitch gives an "acid number" * varying from about 9—23 and an "ester number" from 9—16; the corresponding numbers for a petroleum pitch vary between 0.6 and 3.0 and 3.4 and 5.9.

In the titrations the authors have used a 2 per cent. solution of alkali-blue-6b as indicator.

When the hard fatty pitches are distilled with superheated steam (300°), or even simply distilled, the first distillates always contain appreciable amounts of acid. The authors find that all fatty pitches contain small amounts of copper soaps, obtained from the copper vessels in which the distillation has been carried out. Petroleum pitches, on the other hand, are free from copper.

J. J. S.

New Colour Reaction for Distinguishing between certain Isomeric Allyl and Propenyl Phenols. By ALFRED C. CHAPMAN (*Analyst*, 1900, 25, 313—314).—The reaction is brought about by dissolving 1 c.c. of the phenol in 5 c.c. of acetic anhydride and then adding a fragment of fused zinc chloride or one drop of sulphuric acid.

Eugenol gives, with sulphuric acid, a brown coloration which quickly turns purple and finally wine-red; with zinc chloride, a transitory pale yellow. *iso*Eugenol gives, with sulphuric acid, a rose-pink coloration quickly changing to a light brown; with zinc chloride, a bright rose-pink. Safrole gives, with sulphuric acid, a bright emerald green coloration, becoming brownish-green and finally brownish; with zinc chloride, a pale blue, fading after a time and finally turning light

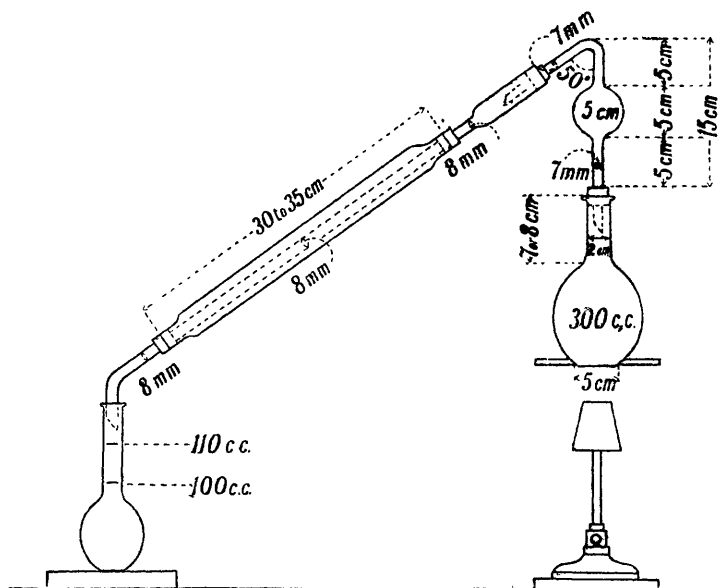
* The acid number indicates the number of milligrams of potassium hydroxide required to neutralise the acid contained in 1 gram of the substance; the ester number gives the number of milligrams of potassium hydroxide required to hydrolyse the esters contained in 1 gram of the substance.

brown. *iso*Safrole gives, with sulphuric acid, a faint, transient pink coloration, turning reddish after a time; with zinc chloride, a pink becoming brownish-pink, and finally brown. Estragol gives, with sulphuric acid, a purple coloration turning to indigo blue and then to bluish-purple; with zinc chloride, a blue-violet, becoming deep mauve and finally brownish. Anethole gives, with sulphuric acid, no coloration at first, but after a short time a yellowish tinge; with zinc chloride, a pale yellow, appearing slowly and deepening on standing, finally becoming brick-red.

Every possible care was taken to ensure the purity of the phenols used in the experiments.

L. DE K.

The Margarine Clause of the Food and Drugs Act. [By THOMAS E. THORPE, WALTER W. FISHER, ALFRED H. ALLEN, EDWARD J. BEVAN, and OTTO HEHNER] (*Analyst*, 1900, 25, 309—313).—A report as to the manner of estimating the proportion of butter fat in margarine, which has been agreed to by the Principal Chemist of the



Government Laboratory and a Committee appointed by the Society of Public Analysts. The method recommended is as follows:

Five grams of the melted and filtered sample are introduced into a 300 c.c. flask (see Fig.), 2 c.c. of aqueous sodium hydroxide (1 : 1) free from carbon dioxide are added, and also 10 c.c. of 92 per cent. alcohol, and the mixture is heated under a reflux condenser, connected with the flask by a T-piece, for 15 minutes in a bath containing boiling water. The alcohol is distilled off by heating the flask on the water-bath for about half an hour, or until the soap is dry. One hundred c.c. of hot water which has been kept boiling for at least 10 minutes are

added, and the flask heated until the soap is dissolved. Forty c.c. of *N*-sulphuric acid and three or four fragments of pumice or broken pipe-stems are added, and the flask is at once connected with the condenser, as indicated in the figure. The flask, which is supported on a circular piece of asbestos 12 cm. in diameter having a hole in the centre 5 cm. in diameter, is first heated with a very small flame, to fuse the insoluble fatty acids without causing the liquid to boil. The heat is then increased, and when fusion is complete 110 c.c. are distilled off into a graduated flask, the distillation lasting about 30 minutes (say from 28 to 32 minutes). The distillate is shaken, 100 c.c. are filtered off, transferred to a beaker, 0.5 c.c. of phenolphthalein solution (1 gram in 100 c.c. of alcohol) added, and the filtrate titrated with *N*/10 sodium or barium hydroxide. As the chemicals used may yield a slightly acid distillate, a blank experiment should be made, and the result allowed for; this should, however, not exceed 0.3 c.c. of *N*/10 alkali. The final result multiplied by 1.1 is the Reichert-Wollny number.

The following table gives, I, the Reichert-Wollny number as determined by this method, and, II, the corresponding amount of butter fat that is assumed to be present in the margarine.

| | | | | | | | | | | | |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| I. | 4.0 | 4.3 | 4.6 | 4.9 | 5.2 | 5.5 | 5.9 | 6.2 | 6.5 | 6.8 | 7.1 |
| II. | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |

No presumption against the margarine in regard to its content of butter fat should be raised unless the Reichert-Wollny number thus ascertained exceeds 4.

L. DE K.

Ceylon Oil in Margarine and Butter. By W. G. A. INDEMAN (Chem., Centr., 1900, ii, 1134; from *Ned. Tydschr. Pharm.*, 12, 306—310).—The presence of Ceylon oil in butters or margarines renders analysis more difficult on account of the considerable amount of volatile fatty acids which it yields. The adulteration may, however, be detected by combining the Reichert-Meissl number with the refractometer number as shown in the following table:

| | Reichert-Meissl number. | Refractometer number. |
|--|----------------------------|--------------------------|
| Pure butter..... | 27.13 | 46.25 |
| Same adulterated with 20 per cent. of foreign fat | 21.15 | 45.5 |
| Margarine No. 1..... | 5.87 | 43.5 |
| Margarine No. 2..... | 5.16 | 44.5 |
| Ceylon oil..... | 7.60 | 36.0 |
| Margarine without Ceylon oil..... | 1.32 | 54.0 |

L. DE K.

Estimation of Fat in Fæces. By OEFLE (Chem. Centr., 1900, ii, 1137; from *Pharm. Centr. Halle*, 41, 649—651).—The estimation of the fat in the portion of the ethereal extract which is insoluble in water by assuming its saponification number to be 200 is quite untrustworthy; to obtain results which agree with the gravimetric estimation of the fatty acids, the saponification number must be supposed to vary from 92 to 350.

It is recommended to estimate the fat by its ether-number, by

weighing, and by titration so as to get both the normal fat and the fatty acids. L. DE K.

Analytical Chemistry of the Alkaloids. V. Employment of Tannic Acid for Purifying Alkaloid Residues in Chemico-toxicological Analysis. By KARL KIPPENBERGER (*Zeit. anal. Chem.*, 1900, 39, 627—633).—Salkowski's objections (*Abstr.*, 1898, ii, 547) to the author's "glycerotannic acid" method (*Abstr.*, 1895, ii, 465) are admitted, as far as regards the behaviour of Witte's peptone with this reagent, but if the extraction be made at 40° as recommended, none of the proteids present in cadaveric matter will pass into solution, and to the objection that the alkaloid tannates may be partially precipitated by diluting the glycerol solution with much water, it is replied that this occurs only in the absence of acid. The author originally proposed the addition of tartaric acid; hydrochloric acid is even better. He, however, admits that the extraction of the glycerol solution by chloroform is an inconvenient operation. On the other hand, Salkowski's proposal to treat the alkaloid tannates with hide powder does not succeed in the case of alkaloids, such as brucine, which form very insoluble tannates. A more convenient solvent than glycerol for the alkaloid tannates is found in acetone, in which the freshly precipitated tannates of brucine, strychnine, atropine, morphine, aconitine, veratrine, papaverine, narceine, thebaine, codeine, emetine, nicotine, coniine, sparteine, quinine, narcotine, and cocaine dissolve readily. The majority of the proteid tannates, including Witte's peptone, are insoluble in acetone, although there exist commercial peptones, of which traces dissolve. The presence of hydrochloric acid is to be avoided when extracting with acetone. Having obtained the acetone solution, a small quantity of glycerol and some dilute hydrochloric acid should be added before evaporating the acetone, and an aqueous solution is then obtained which is well suited for the extraction with chloroform. The acetone method is of course useless where volatile alkaloids have to be searched for.

M. J. S.

Estimation of Proteids in Fodder. By HENRIK SCHJERNING (*Zeit. anal. Chem.*, 1900, 39, 633—639).—The author has now applied his method of precipitation by uranium acetate (*Abstr.*, 1898, ii, 658; 1900, ii, 779) to the estimation of the total proteids in various feeding stuffs, in comparison with Stutzer's method, which has generally been employed for the purpose. In consequence of the absence from most fodders of the peptones which Stutzer's reagent fails to precipitate, the two methods give in most cases closely concordant results. In the case of sunflower-seed cake and cotton-seed cake Stutzer's reagent gave slightly the higher numbers, a result which is probably due to the precipitation of amino-compounds. Special experiments showed that the uranium process was not interfered with by the presence of such non-proteid nitrogenous substances as piperazine, arginine, asparagine, &c. The estimation is carried out as follows: 0.5—1 gram of the substance is digested at the ordinary temperature with 100 c.c. of water for 20 hours; the mixture is then heated to 50°, and 20 to 40 c.c. of saturated solution of uranium acetate (which should be free

from basic salt) are added. The mixture is kept at 50° for half an hour, direct light being excluded, and the precipitate collected on an extracted filter and washed with a cold 1—2 per cent. solution of uranium acetate. It is then evaporated nearly to dryness with addition of a little magnesia (Abstr., 1900, ii, 780) and the nitrogen is estimated by Kjeldahl's process, adding 0.1 c.c. of *N*/10 acid for every 100 c.c. of filtrate. M. J. S.

Uniformity in Soil Analyses. By A. D. HALL (*Analyst*, 1900, 25, 281—286).—Recommendations of the Committee of the Agricultural Education Association, having for their object the securing of a certain uniformity in soil analyses.

1. *Taking sample.*—This should be taken at a depth of 9 inches, but in the case of shallow soils at such a depth as marks a natural line of demarcation. 2. *Drying.*—The sample should be air-dried. The drying may be accelerated by warming for some time at 40°. 3. *Sifting.*—A sieve with round holes 3 mm. in diameter should be used to separate the fine earth from the stones and gravel. Aggregates of clay and silt may be broken up with a wooden pestle, but stones or lumps of chalk should not be crushed. For the determination of the available constituents, the fine earth is used without grinding, but in other cases it is sifted through a woven sieve of 40 meshes to the inch, or a sieve with round holes of 1 mm. in diameter. 4. *Estimation of moisture.*—The sample should be dried in the steam-oven to constant weight. 5. *Determination of loss on ignition.*—The result should be corrected for moisture and for any carbon dioxide expelled from the carbonates. 6. *Determination of nitrogen.*—Kjeldahl's process should be used. 7. *Determination of calcium carbonate.*—This is calculated from the carbon dioxide evolved when the fine earth is treated with an acid, no discrimination being made between calcium and magnesium carbonate. 8. *Determination of total mineral constituents.*—The fine earth is first boiled with strong acid in an open flask and then digested in a loosely-stoppered flask on the water-bath for 40—48 hours. In this solution, the phosphoric acid, potash, and, if necessary, other mineral constituents are determined. 9. *Determination of available phosphoric acid and potash.*—Dyer's citric acid process (*Trans.*, 1894, 65, 115) is recommended. 10. *Expression of results.*—Unless otherwise stated, results should be expressed as percentages calculated on the fine earth in an air-dry state.

Experiments have been made with the object of supporting these recommendations. It has been found that hydrochloric acid acts more satisfactorily than nitric acid. As a rule, the ignited soil yielded more potash and less phosphoric acid than the raw sample.

L. DE K.

General and Physical Chemistry.

Lamps for Spectra. III. By ERNST BECKMANN (*Zeit. physikal. Chem.*, 1900, 35, 652—660).—The paper contains a description and an illustration of an elaborate lamp constructed on the lines previously indicated (Abstr., 1900, ii, 701; this vol., ii, 53), and suitable for all sorts of spectroscopic investigations. In another lamp, capable of giving monochromatic light for polarimeter and refractometer work, the flame is circular, and the spray is produced either electrolytically or with the porous porcelain tube previously described. To secure an intense sodium flame, hydrogen should be substituted for coal gas, and the salts used should be those which readily give up oxygen, namely, chlorate, perchlorate, nitrate, or peroxide. J. C. P.

Arc Spectra of some Metals as Influenced by an Atmosphere of Hydrogen. By HENRY CREW (*Phil. Mag.*, [v], 50, 497—505).—It was found that arc spectra of metals are modified when the arc is formed in an atmosphere of hydrogen, some of the lines being enhanced, some weakened, and others not affected. The modifications of zinc and magnesium spectra and for a portion of the iron spectra are indicated by tables. From these, it is observed that all the lines in the arc spectrum which are affected by the hydrogen atmosphere belong also to the spark spectrum, whilst, on the contrary, those lines which belong to Kayser and Runge's series are not affected. L. M. J.

Differences of Potential between Metals and Non-aqueous Solutions of their Salts. II. By LOUIS KAHLENBERG (*J. Physical Chem.*, 1900, 4, 709—714. Compare Abstr., 1899, ii, 624).—The E.M.F.'s of a number of non-aqueous concentration cells were determined; the ratio of the ion concentrations in the solutions were calculated from the molecular conductivities and the E.M.F.'s calculated by the well-known Nernst formula: $\pi = RT/ne \cdot \log c_1/c_2$. The cells employed were (1) $\text{Ag.N}/10\text{AgNO}_3.\text{N}/100\text{AgNO}_3.\text{Ag}$; (2) $\text{Ag.N}/10\text{AgNO}_3.\text{N}/500\text{AgNO}_3.\text{Ag}$;

(3) $\text{Ag.N}/10\text{AgNO}_3.\text{N}/1000\text{AgNO}_3.\text{Ag}$, in pyridine solutions; (4) $\text{Ag.N}/8\text{AgNO}_3.\text{N}/128\text{AgNO}_3.\text{Ag}$ in acetonitrile; (5) $\text{Cd.N}/48.9\text{CdI}_2.\text{N}/214.7\text{CdI}_2.\text{Cd}$ in acetonitrile. The determinations gave the following values in volts for the E.M.F. (1) 0.035, (2) 0.061, (3) 0.076, (4) 0.046, (5) 0.032, whilst those calculated were (1) 0.052, (2) 0.085, (3) 0.099, (4) 0.050, (5) 0.017 volt. Owing to these discrepancies, the author considers that Nernst's expression cannot be applied to non-aqueous solutions, and considers it desirable that the formula should be subjected to rigid tests in aqueous solutions (compare, however, Jahn, Abstr., 1900, ii, 707). L. M. J.

The Chlorine-Hydrogen Gas Cell. By IWAN AKUNOFF (*Zeit. Elektrochem.*, 1900, 7, 354—356).—The author finds the E.M.F. of the hydrogen-chlorine gas cell (the electrolyte being 3-normal hydrochloric acid saturated with potassium chloride) to be 1.37125—0.000855*t* volts

From this result, the heat developed by the reaction which gives rise to the E.M.F. is calculated by means of Helmholtz's formula to be 37,107 cal. The heat of formation of hydrochloric acid in the above-mentioned solution from gaseous hydrogen and chlorine at constant pressure is 37,680 cal.

Müller (*Zeit. Elektrochem.*, 1900, 6, 573) has supposed the reaction to be $\text{H}_2 + \text{HClO} = \text{H}_2\text{O} + \text{HCl}$; this would, however, develop 38,850 cal. It is therefore probable that the E.M.F. of the cell is due to the direct union of hydrogen and chlorine. T. E.

Poynting's Theorem. By P. S. WEDELL-WEDELLSBORG (*Zeit. physikal. Chem.*, 1900, 35, 604—607).—A criticism, from a purely physical standpoint, of Mie's paper (*Abstr.*, 1900, ii, 703), and a summary of the differences between the author's views and those of Poynting and Thomson. J. C. P.

Electrical Conductivity of Aqueous Solutions of Alkali Chlorides and Nitrates. By FRIEDRICH KOHLRAUSCH and MARGARET E. MALTBY (*Wiss. Abhandl. phys.-tech. Reichsanstalt*, 1900, 3, 155—227).—An account of this work has already appeared (see *Abstr.*, 1900, ii, 61), but the present paper contains very much fuller details of the experimental data. J. C. P.

Electromotive Force and Optical Constants of Chromium. By F. JULES MICHELI (*Chem. Centr.*, 1900, ii, 809; from *Arch. Sci. phys. nat. Genève*, [iv], 10, 122—131).—When the metals are arranged in the order of their electromotive efficiency, chromium in the inactive condition stands near platinum, in the active condition immediately after zinc (compare Hittorf, *Abstr.*, 1898, ii, 363; 1900, ii, 127). Optical investigation must throw light, as in the case of iron, on the question whether the existence of the active and inactive states is due to two different modifications of chromium, or to a superficial layer of oxide in the latter case. The author finds, by an optical method, that there is no such layer of oxide formed. According to Hittorf and to Ostwald (*Abstr.*, 1900, ii, 730; this vol., ii, 24), chromium which has been rendered active becomes inactive if left exposed to the air; the author, on the other hand, finds that chromium which has been rendered inactive gradually assumes the active condition. According to Hittorf, the activity of chromium can be increased by immersion in fused zinc chloride; optical investigation reveals, in this case, the presence of a coating of oxide; subsequent immersion in nitric acid renders the chromium inactive, without in any way affecting the layer of oxide. J. C. P.

Concentration at the Electrodes in a Solution, with special reference to the Liberation of Hydrogen in the Electrolysis of a Mixture of Copper Sulphate and Sulphuric Acid. By HENRY J. S. SAND (*Compt. rend.*, 1900, 131, 992—995; *Phil. Mag.*, 1901, [vi], 1, 45—79).—An expression is deduced for the concentration at an electrode of infinite area, in terms of the time, current, and diffusion coefficient. In mixtures, however, a formula cannot be deduced, but limiting values may be calculated between which the actual concentration should lie. These were applied to

calculate the time in which the concentration of copper at an electrode in a mixture of copper sulphate and sulphuric acid would become zero, and the liberation of hydrogen would hence commence. The observed time was found in all cases to lie between the calculated limits. The calculations assume the absence of convection currents, the liberation of hydrogen being completely prevented by vigorous stirring

L. M. J.

Electro-capillary Properties of Mixtures, and Electro-capillary Viscosity. By A. GOUY (*Compt. rend.*, 1900, 131, 835—837).—If the curves for electro-capillarity against potential difference be taken in the case of (1) an aqueous solution of a pure compound *A*, and (2) the same solution to which a small quantity of a second compound, *B*, is added, it is found that in general these coincide for strong negative polarisations. If, however, the compound *B* is an 'active' compound, for example, an iodide or bromide, a variation of the maximum occurs, and near the maximum the curve resembles that of the solution of *B*, even though its concentration be very small compared with that of *A*. This variation of the maximum may attain the value of 0.2 volt, so that the maximum value does not always correspond with zero difference of potential. In these mixtures also, the mercury only slowly reaches its stable position and this effect, which the author terms electro-capillary viscosity, is explained by the supposition of the accumulation at the mercurial surface of the 'active' anions, the slow establishment of equilibrium being due to the slight concentration of these in comparison with the other ions.

L. M. J.

Measurement of the Velocity of Gaseous Evolutions. Application to the Voltameter. By ANDRÉ JOB (*Bull. Soc. Chim.*, 1901, [iii], 25, 7—9).—If a gas is allowed to escape through a long capillary tube from the vessel in which it is being evolved, the excess of the pressure of the gas in the vessel over that of the external air is a measure of the rate of evolution of the gas at any instant. Use may be made of this principle in the continuous study of processes of fermentation, of the dissolution of metals in acids, and of other reactions in which gases are evolved; the method has been recently employed by Ostwald (this vol., ii, 24) and Bredig and Hahn (*Zeit. Elektrochem.*, 1900, 7, 254) for such purposes. A voltameter, when provided with a water manometer and a capillary exit tube, becomes virtually an amperemeter, the excess of pressure being proportional to the rate of evolution of gas, and hence also to the intensity of the current, at any instant.

N. L.

Magnetism and Atomic Weight. By LEO ERRERA (*Bull. Roy. Acad. Belg.*, 1900, 152—161).—The author reviews critically the work of Königsberger (*Ann. Phys. Chem.*, 1898, [ii], 66, 698) and Meyer (*Abstr.*, 1899, ii, 587; 1900, ii, 7). It is simpler to connect the magnetism of the elements directly with their atomic weight, rather than with their atomic volume, and a table is drawn up showing the connection referred to.

J. C. P.

Thermal and Electrical Conductivity, Thermal Capacity, and Thermo-electric Efficiency of some Metals. By WILHELM JAEGER and H. DIESELHORST (*Wiss. Abh. phys.-tech. Reichsanstalt*, 1900, 3, 269—424).—The chief result of this exhaustive investigation is the confirmation of the law of Wiedemann and Franz for copper, silver, gold, nickel, zinc, cadmium, lead, and tin. For these metals, the ratio λ/K , where λ is the thermal and K the electrical conductivity, is, as required by the law, constant, although considerable deviations are found in some cases. The law of Lorenz is also applicable, according to which the above ratio is proportional to the absolute temperature. The exceptionally high value of the ratio in the case of iron is attributed to impurity (compare Grüneisen, *Ann. Phys.*, 1900, [iv], 3, 43). This is borne out by the investigation of alloys, for when a metal B is added to a metal A , the ratio λ/K for the alloy is greater than for the pure metal A . Platinum and palladium are peculiar in giving an exceptionally large value both for the ratio λ/K and its temperature coefficient. Aluminium shows a low value of the ratio λ/K , but a large temperature coefficient, whilst the opposite holds for bismuth.

J. C. P.

Thermal and Electrical Conductivity of Copper-Phosphorus and Copper-Arsenic. By A. RIETZSCH (*Ann. Phys.*, 1900, [iv], 3, 403—427).—By the introduction of small quantities of phosphorus and arsenic, the thermal conductivity (λ) of copper is diminished more than is its electrical conductivity (K). Thus if for pure copper both λ and K are put = 100, then for an alloy containing 0.87 per cent. of phosphorus $\lambda = 16$, $K = 20.6$, and for one with 5.25 per cent. of phosphorus, $\lambda = 4$, $K = 5.6$. Similar series of numbers are obtained for copper-arsenic. The influence of non-metals on the conductivities (thermal and electrical) of metals is opposite to that of other metals (compare preceding abstract).

J. C. P.

Molecular Specific Heats of Dissociable Gaseous Compounds. By A. PONSOT (*Compt. rend.*, 1900, 131, 990—992).—A mathematical paper, in which the author deduces that at extreme limits of rarefaction the molecular specific heat of a gaseous compound is less than that of the mixture of its dissociation products, whether at constant pressure or constant volume; in the latter case, the difference may be regarded as approximately zero.

L. M. J.

Air Thermometer at High Temperatures. By LUDWIG HOLBORN and ARTHUR DAY (*Ann. Phys.*, 1900, [iv], 2, 505—545).—The authors have studied the conditions which must be observed if a gas thermometer is to be used with confidence at high temperatures. The reservoir should be of platinum-iridium, and nitrogen should be used as the expanding gas. With this standard gas thermometer, they have compared a platinum-platinum rhodium thermo-couple, the E.M.F. of which, for the temperature interval of the experiments, 300—1150°, is given by an equation of the second degree. This thermo-couple was further used to determine the melting points of several metals by one of two methods. Either a short wire of the metal under observation was introduced into the junction of the thermo-

couple, and the E.M.F. noted at the time of its fusion, or a larger quantity was put in a crucible, and the thermo-element, protected by a porcelain tube, immersed in the fused metal.

The following melting points were determined :

| | | | |
|---------------------------------|---------|-------------------------|--------|
| Gold (wire method)..... | 1064·0° | Antimony (crucible) ... | 630·5° |
| Silver (wire method) | 953·6 | Aluminium (crucible) .. | 657·3 |
| Silver (crucible, air admitted) | 954·9 | Zinc (crucible) | 419·0 |
| Silver (crucible, air excluded) | 961·5 | Lead (crucible) | 326·9 |
| Copper (oxidising atmosphere) | 1065·0 | Cadmium (crucible) ... | 321·7 |
| Copper (reducing atmosphere) | 1084·0 | | |

The authors consider that up to 1150° the correct temperature can be determined to within 1° with the use of a thermo-couple. The melting points of the metals, as above determined, are compared with the values obtained by Heycock and Neville (*Trans.*, 1895, **67**, 160, 1024), and Callendar (*Phil. Mag.*, 1899, [v], **48**, 519). J. C. P.

Melting Point of Gold. By LUDWIG HOLBORN and ARTHUR DAY (*Ann. Phys.*, 1901, [iv], 4, 99—103).—The melting point of gold as determined by the crucible method (see preceding abstract) is 1063·5°. The value obtained by the wire method for the same sample is 1063·9°. The authors think that in standardising thermo-couples the wire method may advantageously be used for determining the melting point of gold. J. C. P.

Change of Temperature attending the Solidification of Melted Organic Substances. By BRONISLAW PAWLEWSKI (*Ber.*, 1900, **33**, 3727—3731).—The substance (5 grams) was placed in a test-tube so as to surround the bulb of a thermometer; this tube was placed in a wider one. The temperature was then raised, by means of a gas burner, to 20—40° above the melting point of the substance, the apparatus allowed to cool, and the temperature read every 20 seconds and plotted against the time. Three types of curves were obtained; in the first, the temperature falls rapidly, then remains constant for a time, and finally falls again; in the second, it falls rapidly, then more slowly for a time, and finally more rapidly again; in the third, it falls rapidly, the substance becoming overcooled (in one case by as much as 40°), then rises rapidly as the substance solidifies, keeps constant for a time, and finally falls once more. The interval of constant temperature, or that where the fall is slow, is in all cases below the melting point observed in a capillary tube.

To the first type belong *p*-dichlorobenzene, *p*-dibromobenzene, *p*-chloronitrobenzene, *p*-nitrophenol, *p*-toluidine, *ω*-dichloroxylylene, *m*-nitroaniline, triphenylmethane, diphenyl, naphthalene, acenaphthene, stearic acid, phenylacetic acid, catechol, benzamide, methyl oxalate, azobenzene, formanisidine, acetanilide, diphenylamine, β -naphthol, β -naphthylamine, &c. To the second, camphoroxime, benzyaniline, guaiacol, anisic acid. To the third, benzil, benzoin, benzylideneacetone, chloroacetic acid, *m*-nitrochlorobenzene, chloral hydrate, *p*-chloroaniline, *p*-toluonitrile, α -naphthylamine, vanillin, coumarin, phenol, phthalide, formanilide, resorcinol, acetyldiphenylamine, &c. C. F. B.

Cryoscopic Researches. By PAUL CHRUSTCHOFF (*Compt. rend.*, 1900, 131, 883—886).—In view of many discrepancies in cryoscopic observations, a new method was employed in which the temperatures were taken by a Callender and Griffiths' thermometer, the position along the wire of the Wheatstone bridge being read by a micrometer eyepiece; a displacement of 0.2 mm. along the wire indicated a difference of temperature of 0.001°. The usual precautions regarding stirring, &c., were observed, and the observed depressions are given in scale readings, not in degrees, the rates of these depressions to concentration being recorded. It is found that this ratio remains constant on dilution for sodium chloride, decreases for potassium bromide, and increases for sucrose and for potassium sulphate. L. M. J.

Dupré-Rankine Vapour Tension Law. By PAUL JULIUSBURGER (*Ann. Phys.*, 1900, [iv], 3, 618—659).—The law is expressed in the equation $\log P = A - B/T - C \log T$, and the author finds that the various ways of deducing it are all equally valid. Theoretically, the law holds strictly only when the tension is small, but practically it is applicable over a wide range, for some substances even up to the critical temperature. The formula may also be used in cases where P is the dissociation pressure of a system. J. C. P.

Vapour Tension of Water at Temperatures between -12° and 25°, especially at 0°. By MAX THIESEN and KARL SCHEEL (*Wiss. Abh. phys.-tech. Reichsanstalt*, 1900, 3, 71—94).—The mean value of the vapour tension of water at 0°, as determined in a number of very careful measurements, is 4.575 mm. J. C. P.

Experiments on Fractional Distillation. By SYDNEY YOUNG (*J. Soc. Chem. Ind.*, 1900, 19, 1072—1075).—The rate at which a mixture is distilled largely influences the extent of the separation effected; for efficiency, the number of drops per minute should not exceed 60, and good contact should be ensured between the ascending vapour and the condensed liquid (compare *Trans.*, 1899, 75, 679). The value of plotting curves between the weight of each fraction and its temperature range as a means of recognising the boiling point of the ingredients of a mixture, is discussed with reference to a former paper (Thomas and Young, *Proc.*, 1895, 172); the isolation of hexamethylene from American petroleum is also dealt with (compare Fortey, *Trans.*, 1898, 73, 932).

A method is described for ascertaining approximately, without completely separating them, the proportion of the constituents of a liquid mixture, for instance, one containing 31.7 per cent. of methyl acetate, 38.2 of ethyl acetate, and 30.1 of propyl acetate; the boiling points of the esters are 57.1°, 77.15°, and 101.55°, and the two middle points 67.1° and 89.35°. It is found that after a few fractionations the percentage of the mixture boiling below 67.1° remains constant (30.5 per cent.), and represents the proportion of methyl acetate; the proportion boiling below 89.35° is also constant, namely 69.3 per cent., and 69.3—30.5 or 38.8 represents the proportion of ethyl acetate present, whence by difference the amount of propyl acetate is 30.7 per cent. This method is shown to hold for other homologues (for instance,

benzene and toluene, mixed in the proportions 1:9 and 9:1), but additional experiments will be necessary to ascertain whether it is available for substances which are not homologous. It is essential that the rate of distillation should remain nearly constant.

W. A. D.

Distillation in a Vacuum with Hempel's Dephlegmator. By WILHELM HIRSCHL (*Chem. Centr.*, 1900, ii, 1193—1194; from *Oesterr. Chem. Zeit.*, 3, 517).—When Hempel's dephlegmator is used for the distillation of liquids in a vacuum, the usual tendency of the liquid to accumulate in the glass beads instead of running back into the flask becomes so marked that satisfactory distillation is often impossible. This disadvantage may be avoided by inserting a platinum spiral in the wider tube and of the same diameter in such a way that the glass beads are raised and do not rest directly on the constricted portion; the lower tube also requires to be at least 15 mm. in diameter and is fused on to the neck of the distilling flask.

E. W. W.

Determination of Vapour Density under Reduced Pressure. By CARL SCHALL (*J. pr. Chem.*, 1900, [ii], 62, 536—542. Compare Bleier and Kohn, *Abstr.*, 1899, ii, 643).—This paper contains the discussion of a formula for the calculation of K , a constant of the apparatus employed by the author for the determination of vapour density under diminished pressure (*Abstr.*, 1889, 331).

E. G.

Vapour Pressure of a Series of Benzene Compounds. By BENEDIKT WORINGER (*Zeit. physikal. Chem.*, 1900, 35, 723—724).—A reply to Winkelmann's criticism (this vol., ii, 57) of the author's previous work (*Abstr.*, 1900, ii, 709).

J. C. P.

Exact Relation between Osmotic Pressure and Vapour Pressure. By ARTHUR A. NOYES (*Zeit. physikal. Chem.*, 1900, 35, 707—721. Compare *Abstr.*, 1897, ii, 395; 1899, ii, 357).—The exact thermodynamical relation between the osmotic pressure P_1 and the vapour pressure p_1 of a solution, is given by the equation

$$\int_{p_1}^{p_0} v \cdot dp = (P_1 + p_0 - p_1) V_0 \left[1 + \frac{k_0}{2} (P_1 + p_0 - p_1) \right], \text{ where } p_0, V_0, k_0, \text{ are}$$

respectively the vapour pressure, the specific volume, and the coefficient of compressibility of the liquid solvent. The only supposition made in the deduction of this equation is that k_0 is constant between the pressures p_0 and $p_1 - P_1$. Seeing that the latter pressure is generally negative, the value of k_0 has to be got by extrapolation, a process which is justified especially by the work of Worthington (*Phil. Trans.*, 1893, 183, 355). From the above equation, it follows that to calculate the osmotic pressure from the vapour pressure integral, the latter should be divided by the ordinary specific volume of the solvent, and not, as is usually done, by the volume change of the solution. In the course of the paper, the author replies to the criticism of Dieterici (*Abstr.*, 1899, ii, 547).

J. C. P.

Osmotic Pressure of Complex Solutions. By ALEXANDER A. JAKOWKIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 721—727).—From

theoretical considerations, the author arrives at the following expression, which relates to the osmotic pressure of a solution of a substance in a mixture of two solvents: $(P_0/P)^m = (p_0/p)^M$, where p represents the partial pressure of one of the solvents for the solution, determined in a Pfeffer's cell, p_0 its partial pressure for the complex solvent, and m the molecular weight of the solvent in the gaseous state; P , P_0 , and M represent the corresponding magnitudes for the second solvent. The above expression simplifies to: $P_0/p_0^k = P/p^k$, where k stands for the ratio of the molecular weights of the two liquids, $M:m$.
T. H. P.

Theory of the Capillary Layer between the Homogeneous Phases of Liquid and Vapour. By G. BAKKER (*Zeit. physikal. Chem.*, 1900, 35, 598—603).—A mathematical paper, unsuitable for abstraction.
J. C. P.

Dissociation of Antimony Pentachloride. By MARCEL NOTHOMB (*Bull. Roy. Acad. Belg.*, 1900, 551—558).—The normal vapour density of antimony pentachloride is 10.35, but in the interval 180—360°, the value obtained by Victor Meyer's method, gradually falls from 7.58 to 5.34. The application of Planck's law to this case leads to the equation $c_2^2/c_1 = a.e^{-\frac{b}{\theta}} \cdot \theta/p$, where c_1 and c_2 are the concentrations of the undissociated molecules and the products of dissociation respectively, θ is the absolute temperature, p is the pressure in mm. of mercury, a and b are constants. The values calculated for the dissociation by this equation agree closely with those actually obtained.
J. C. P.

Reaction Velocity and Equilibrium. By WILDER D. BANCROFT (*J. Physical Chem.*, 1900, 4, 705—708).—Abnormal reaction velocities have been explained by the assumption that the reaction proceeds in two or more stages, on one only of which depends the experimentally found velocity. Inasmuch as this has not hitherto been found in the case of a reversible reaction, it is sometimes assumed that irreversibility is a necessary condition for the production of these abnormal velocities. Suppose, however, a reversible reaction is represented by the equation $2A + B = A_2B$; the equilibrium equation is then $x = k(A-x)^2(b-x)$. If, however, the reaction proceeds in two stages $A + B = AB$; $AB + A = A_2B$, then the final equilibrium is given by $x = k(a-x-y/2)^2(b-x-y)$, and since the intermediate product is finally of concentration practically zero, this reduces to the first expression, so that the equilibrium result would lead to an equation of the third order, although the reaction velocity might be of the second order, and abnormal velocities may occur in reversible reactions. The author hence protests against the practice of deducing equilibrium relations from reaction velocities instead of solely from the stoichiometric relations.
L. M. J.

Velocity of Intramolecular Migration of Bromoamides under the Influence of an Alkali. By W. VAN DAM and J. H. ABERSON (*Rec. Trav. Pays. Bas.*, 1900, 19, 318—331).—The transformation of bromoamides under the influence of potassium hydroxide

has been previously found to be a reaction of the first order (van Dam, *Abstr.*, 1900, i, 171). This indicates that the transformation is really an intramolecular change and not a reaction between two molecules. The effect of concentration of alkali was investigated, and it was found that for concentrations above $N/2$ the curve for velocity constant against concentration was a straight line. For lower concentrations, however, the velocity constant increases during the progress of the reaction, and it was found that a different reaction also proceeds by which benzoylphenylcarbamide is produced. The action of primary and secondary amines was also investigated; these were found to occasion condensation without the formation of aniline, but values for a reaction velocity constant were not obtained. The effect of temperature between 16° and 33° was found to be in accord with Arrhenius' formula, $\log k_1/k_2 = A.(T_1 - T_2)/T_1.T_2$, the value for A being 14.48. The velocity constants for $N/4$ potassium, sodium, and lithium hydroxides are in the ratio 175 : 166 : 158, the conductivities of the same solutions being in the ratio 175 : 154 : 140; on the same scale, the values for barium and strontium hydroxides are 169 and 169, but lack of data prevent the comparison with conductivity.

L. M. J.

Inversion of Cane Sugar. By EDMUND O. VON LIPPMANN (*Ber.*, 1901, 33, 3560—3564).—A criticism of the theories of Arrhenius (*Abstr.*, 1889, 1103; 1899, ii, 359), Rothmund (*ibid.*, 1896, ii, 593), Sigmund (*ibid.*, 1899, ii, 146), and Euler (*ibid.*, 1900, ii, 269).

A. L.

Theory of Solutions. By GUSTAV JAUMANN (*Ann. Phys.*, 1900, [iv], 3, 578—617).—The object of the paper is to make the theory of solutions independent of Arrhenius' ionic hypothesis, and to connect it with the Faraday-Maxwell theory. The author attacks the basis of the molecular theory, and regards Avogadro's hypothesis as unnatural the new basis suggested in the paper involves the introduction of simpler chemical formulæ than are used at present.

J. C. P.

Solvent Action of Vapours. By AZARIAH T. LINCOLN (*J. Physical Chem.*, 1900, 4, 715—731).—The author discusses the question of a solvent action of vapour, and considers it probable that such solvent action exists. The vapour pressure curves for benzoic and salicylic acids were determined between 80° and 190° , and it was found that the acids were present in the vapours passing from saturated solutions boiling at various pressures. No conclusive results concerning a solvent action of the vapour were obtained, however, inasmuch as the quantities of acid present in the vapour were no greater than those corresponding with the vapour pressure of the solid at the temperature of ebullition. To obtain decisive results, experiments at a considerably higher temperature and pressure are necessary.

L. M. J.

Dilute Solutions. By N. TARUGI and GIUSEPPE BOMBARDINI (*Gazzetta*, 1900, 30, ii, 405—420).—The degree of dissociation of a number of aqueous salt solutions of various strengths has been determined, (1) from the depression of the freezing point, (2) from the

lowering of the vapour pressure, and (3) from the electrical conductivity of the solutions. The salts examined were cobalt chloride, ferrous sulphate, and the sulphates of cobalt, nickel, manganese, aluminium, copper, cadmium, sodium, and zinc. The results obtained by the first two methods agree fairly well among themselves, but in some cases differ considerably from those yielded by the third method. The experiments show that nickel, cobalt, and manganese salts can exist completely undissociated in solutions coloured respectively green, red, and pink.

T. H. P.

Size of the Particles present in Colloidal Solutions or pseudo-Solutions. By C. A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1900, 19, 251—258).—According to the laws of optics, the smallest particles capable of polarising the light reflected from them are 50—100 times smaller than the wave-length of light. Assuming a mean wave-length of 0.5μ , the diameter of such particles is therefore $5-10 \mu\mu$. The value deduced in this way from purely physical considerations is in agreement with that calculated from chemical data. Thus, Brown and Millar's researches on starch hydrolysis (*Trans.*, 1899, 75, 331) have led them to assign to soluble starch a molecular weight of about 32,500, and an almost identical result has been arrived at by Rodewald and Kattein (*Abstr.*, 1900, i, 477) from a study of starch iodide. Since van der Waals estimates the diameter of ordinary gaseous molecules as $0.1-0.3 \mu\mu$, and Jäger assigns the value $0.66 \mu\mu$ to the chlorine molecule, it follows, assuming that the specific volumes of the molecules are approximately equal, that the starch molecule has a diameter of about $5 \mu\mu$, as before.

The author comments on the work of previous investigators, and emphasises his opinion that there is no real distinction between true solutions and pseudo- or colloidal solutions. There is no criterion of the homogeneity or heterogeneity of a liquid, and it is possible to pass continuously from undoubted solutions to liquids containing obvious particles in suspension.

N. L.

Method of obtaining Crystals in a Solution without Formation of Superficial Crust. By AUGUSTIN WRÓBLEWSKI (*Bull. Acad. Sci. Cracow*, 1900, 319—325; *Zeit. physikal. Chem.*, 1901, 36, 84—86).—The tube with the solution is closed at the bottom by a membrane of vegetable parchment, and fits tightly in the neck of a surrounding larger bottle, containing pieces of calcium chloride. As the solution is shut off from the air by a U-tube containing water, evaporation takes place only through the parchment, and crystals are formed in the solution when it has become sufficiently concentrated. The method has been successfully applied in the crystallisation of ammonium sulphate and other inorganic compounds, also in the preparation of diastase (compare the author's previous work, *Abstr.*, 1898, i, 500, 713); in this way, crystals of albuminous substances can be obtained in a purer state than by Hoffmeister's method.

J. C. P.

Crystallisation of difficultly Crystallisable Substances. By A. RÜMLER (*Ber.*, 1900, 33, 3474—3475).—Substances which are soluble in water but insoluble in alcohol can be obtained crystalline

by adding alcohol to the aqueous solution until a turbidity appears, filtering, and evaporating slowly in a vacuum over quicklime. By this method, the author has obtained crystals of peptone (prepared from gelatin or from albumin) and of arabic acid from gum arabic.

W. A. D.

Lecture Experiments Illustrating the Electrolytic Dissociation Theory and the Laws of the Velocity and Equilibrium of Chemical Change. By ARTHUR A. NOYES and A. A. BLANCHARD (*J. Amer. Chem. Soc.*, 1900, 22, 726—752; *Zeit. physikal. Chem.*, 1901, 36, 1—27).—Full descriptions are given of seventeen experiments, for the details of which reference must be made to the original.

That colour is an additive property in salt solutions is shown by adding water to alcoholic solutions of copper and cobalt salts. The different rates of double decompositions in inorganic and organic systems are illustrated by the action of silver nitrate on potassium bromide, isopropyl bromide, ethyl bromide, and bromobenzene, all in alcoholic solution. Experiments are described showing the nature of the ions in salt solutions, and their rates of migration during the passage of a current. Simple apparatus serves to show the increase of molecular conductivity with dilution, as well as the different molecular conductivities of equivalent solutions of hydrochloric, sulphuric, monochloroacetic, and acetic acids.

The reaction between potassium iodide and bromate (*Abstr.*, 1896, ii, 470) is used to illustrate the influence of the concentrations of the reacting substances, and the catalytic efficiency of different acids; that the dissociation and consequently the catalytic efficiency of a weak acid is diminished by the addition of a neutral salt may be shown by the same reaction. The influence exerted by strong acids on the dissociation of weak acids is illustrated by several experiments with indicators. When to a saturated solution of a salt *A* a salt *B* with a common ion is added, the salt *A* is partly thrown out of solution; this principle is illustrated by adding either sodium acetate or silver nitrate to a saturated solution of silver acetate.

J. C. P.

New Dropping and Separating Funnels. By P. N. RAIKOW (*Chem. Zeit.*, 1900, 24, 1089—1090).—These funnels are essentially constructed as follows. The top of the stem enters the bulb and represents the outer casing of a stopcock. This has an opening of about 3—4 mm. diameter which is placed so low that the liquid may run completely out of the bulb. To this outer casing is fitted a tube, the upper part of which forms the stopper of the funnel, whilst the lower part forms the tap of the stopcock. The tap has an opening corresponding with the one in the outer casing so that communication may be established at will. There is also a communication between an opening in the neck of the funnel and a channel in the tube which admits the outer air when the funnel is being used. The liquid is introduced through a special opening fitted with a stopper.

Illustrations are given of two kinds of separating funnels which do not greatly differ from each other. The advantage of these funnels is the prevention of loss of liquid by evaporation or leakage through the stopcock.

L. DE K.

Inorganic Chemistry.

Volume of Hydrogen Evolved by the Action of Acids on Granite. A Correction. By ARMAND GAUTIER (*Compt. rend.*, 1900, 131, 1276. Compare Abstr., 1901, ii, 14).—The author corrects his previous statement that 915 c.c. of hydrogen are evolved from 1 kilogram of granite on treatment with acids. The actual volume evolved is much less than this. The higher value was obtained with granite which contained some metallic iron which had been introduced during the pulverisation of the mineral. H. R. LE S.

Molecular Constitution of Water. By WILLIAM SUTHERLAND (*Phil. Mag.*, [v], 50, 460—489).—Assuming the correctness of Mendeléeff's expansion formula $d_t = d_0(1 - at)$, the density curve is a straight line; the density curve for water, however, has a maximum at 4°, but at high temperatures appears to be asymptotic to the straight line for which $a = 0.001$. It is hence considered that this line represents the expansion of one of the ingredients of water, which it is found by extrapolation has at 0° a density = 1.083. Ice probably consists of the other pure constituent, and from analogy with the increase of volume of other solids on fusion, the author calculates that this, when liquid, should have a density of about 0.88. Water at 0° is a mixture of these two, and, assuming no shrinkage occurs, the proportion of the lighter constituent is 0.375. These two constituents are regarded as $(H_2O)_2$ 'dihydrol,' and $(H_2O)_3$ 'trihydrol,' and, by the aid of empirical formulæ, the quantities of 'dihydrol' in water at temperatures from 0° to 200° are deduced. It is shown that these values reproduce fairly satisfactorily the variation of the index of refraction of water with temperature, the values for $(\mu^2 - 1)/(\mu^2 + 2)a$ being 0.20968 for 'trihydrol' and 0.20434 for 'dihydrol.' The compressibility of water and the dissociation of 'trihydrol' into 'dihydrol' by pressure are considered. From the values deduced for the dissociation, it appears that, at about 2300 atmospheres pressure, the 'trihydrol' would be completely dissociated at 0°; this is in accord with the observed fact that at pressures below 3000 atmospheres the anomalies in the expansion curve of water disappear. The surface tension in thin films is, however, sufficient to convert almost the whole of the 'dihydrol' into 'trihydrol' for temperatures below about 60°, and the exceptional properties of solutions in regard to surface tension are probably due to this difference in constitution between the film and the body of water. The latent heat of fusion of ice is largely the heat of dissociation of 'trihydrol' and the high specific heat of water is also due to this factor. Steam consists solely of H_2O , 'hydrol,' and the latent heat of evaporation hence includes the heat of dissociation of 'dihydrol.' The author calculates the thermal values of these dissociation changes, the values obtained being represented by the equations $2H_2O = (H_2O)_2 + 189 \times 2 \times 18$ cal.; and $3(H_2O)_2 = 2(H_2O)_3 + 177 \times 6 \times 18$ cal. The decrease of viscosity of water with pressure is ascribable to the lower viscosity of 'dihydrol,' whilst the anomalous viscosity of many solutions is due to the effect of the solute in increasing the dissociation of 'trihydrol.' These various molecular states

of water are considered from the point of view of the quadrivalency of oxygen and the actual molecular constitutions are discussed. A summary of the various physical constants for 'dihydrol' and 'trihydrol' is given at the end of the paper. L. M. J.

Apparatus for the Evolution of Dry Hydrogen Chloride. By A. GWIGGNER (*Zeit. angew. Chem.*, 1900, 1308—1309).—The apparatus consists of a 10 cm. wide cylindrical generating vessel, the bottom of which is drawn out to a tube 15 mm. wide and 12 cm. long; this cylinder fits by a ground joint into a waste acid vessel, to the bottom of which is sealed a 25 mm. wide beaker, into which the tube passes to a depth of 10 cm. The waste acid vessel has a side opening to carry off the excess of hydrogen chloride which is trapped into a wash bottle containing water. The top of the cylinder, which is 7 cm. wide, is fitted with a ground, tubulated bulb through which passes a pear-shaped separating funnel, and also a side tube fitted with a stopcock as an outlet for the gas; the stem of the funnel is drawn out to a tube 2 mm. wide and slightly bent sideways.

The funnel, which holds about 200 c.c., is filled with strong sulphuric acid. The conical part of the generating cylinder is filled with pieces of glass tubing, on which are placed large lumps of ammonium chloride. By allowing the acid to drop on the lumps and turning the funnel round occasionally, hydrogen chloride is evolved and escapes through the side tube at the top, whilst the solution of the ammonium sulphate runs into the beaker and in the waste acid vessel.

L. DE K.

Autoxidation: Supplementary Note. By FRITZ HABER (*Zeit. physikal. Chem.*, 1900, 35, 608—609. Compare Abstr., 1900, ii, 720).—An acknowledgment that the catalytic influence of benzoic acid on the action of hydrogen peroxide had already been noticed by Engler and Weissberg (Abstr., 1900, i, 399). Schönbein's example of oxidation, $\text{Pb} + \text{O}_2 + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + \text{H}_2\text{O}_2$, is resolved by the author into $\text{Pb} + \text{O}_2 + 2\text{H}^+ = \text{Pb}^{++} + \text{H}_2\text{O}_2$, by an application of the ionic theory to his fundamental conception, the latter being interpreted by the equation: $\text{M} + \text{O}_2 + \text{H}_2\text{O} = \text{MO} + \text{H}_2\text{O}_2$. J. C. P.

The Rendering Active ("Activierung") of Oxygen. By WILHELM MANCHOT (*Annalen*, 1900, 314, 177—199. Compare Manchot and Herzog, Abstr., 1900, ii, 546).—With the object of throwing light on the rendering active of oxygen, the author has studied the oxidation of certain phenols in air. The hydroxy-derivatives of the higher hydrocarbons, which are easily converted into stable products, can be studied with ease, and it is found that hydrogen peroxide is always present at the close of the operation. In the case of the hydroxy-benzenes, a more complicated series of actions takes place. Alkaline quinol, for instance, is converted into quinone and quinhydrone, all three substances absorbing oxygen and producing hydrogen peroxide, which can then act on the materials mentioned. The investigation has been extended to hydrazobenzene, hydrazotriazole, and hydrazomethyltriazole, which, when agitated with barium hydroxide in air, give rise to barium peroxide.

For experimental details and the author's theoretical considerations, reference must be made to the original paper. M. O. F.

Action of Hydrogen Peroxide on Thiosulphates. By ARNOLD NABL (*Ber.*, 1901, 33, 3554—3555).—The author withdraws his previous statement as to this action (compare this vol., ii, 16). The alkaline reaction developed on adding hydrogen peroxide to a solution of sodium thiosulphate, is due to liberation of sodium hydroxide in accordance with the equation $2\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaOH}$, and the green fluorescence in the liquid is probably due to a compound of the litmus with barium tetrathionate. A. L.

Refractive Power of Tellurium in its Compounds. By G. PELLINI and ALFREDO MENIN (*Gazzetta*, 1900, 30, ii, 465—475).—The refractive powers of the following compounds have been measured for the line H_α : (1) tellurium tetrachloride (in benzene); (2) tellurium tetrabromide (in ether); (3) potassium tellurite (in water); (4) telluric acid (in water); and (5) telluriumdiphenyl. Calculation of the atomic refraction of tellurium from these results gives the following mean numbers. According to the Gladstone formula: (1) 32.53, (2) 33.82, (3) 26.10, (4) 24.65, (5) 32.07; for the Lorenz-Lorentz formula: (1) 15.28, (2) 16.66, (3) 17.25, (4) 14.08, (5) 15.52. Thus, for the Gladstone formula, the atomic refraction of tellurium is less in the oxygenated compounds than in the organic and haloid derivatives, a relation which holds also for sulphur and selenium. The difference between the specific refractions of telluric and sulphuric acids (15.57) is almost identical with the difference between those of telluriumdiphenyl and sulphurdiphenyl (15.01). The dispersion of telluriumdiphenyl is high, as is shown by the following numbers: $(\mu_{\text{H}\beta}^2 - \mu_{\text{H}\alpha}^2)/d = 0.02226$ and $(\mu_{\text{H}\beta}^2 - 1)/(\mu_{\text{H}\alpha}^2 - 1) = 1.0778$. T. H. P.

Hydrogen Telluride. By EDMUND ERNYEI (*Zeit. anorg. Chem.*, 1900, 25, 313—317).—Hydrogen telluride mixed with 5—6 per cent. of hydrogen is obtained when tellurium as the negative pole is subjected to a current of 220 volts in an electrolyte of 50 per cent. sulphuric acid. It is essential that the electrolyte should be cooled to -15° or -20° , that organic substances and air should be excluded, and that the mixed gases should be dried at once with calcium chloride and phosphoric oxide. The hydrogen telluride separates in lemon-yellow needles melting at -54° when the mixture of gases is cooled with solid carbon dioxide. It is a colourless, poisonous gas, decomposes immediately in contact with air, or even in a sealed tube, and in two days when kept in a mixture of ice and salt. It burns with a bright blue flame, is somewhat soluble in water, and with potassium and sodium hydroxides yields colourless tellurides which become red and decompose on exposure to the air. It reduces ferric to ferrous chloride and mercuric to mercurous chloride, and decolorises iodine and bromine solutions. The vapour density, determined by Dumas' method, was found to be 65.1 ($\text{H}=1$) or 4.49 ($\text{air}=1$) agreeing with the formula TeH_2 . E. C. R.

Combustion of Nitrogen. By ROBERTO SALVADORI (*Gazzetta*, 1900, 30, ii, 389—404).—In order to obtain the non-absorbable

portion of gas emanating from the earth, the author burns the gas in oxygen in a special apparatus which admits of the products of combustion being absorbed and the residue collected. The combustion takes place in the bulb of an inverted retort, into which the gas is led by a tube which is surrounded by a wider tube for the admission of the oxygen; the products of combustion pass along the neck of the retort into an adapter and thence into the absorbing bulbs, &c. By this means, the whole of the combustible portion of the gas is readily removed, but it is found that when a large excess of oxygen is used, a part of the nitrogen also undergoes combustion. With the same apparatus, a series of experiments has been carried out on the combustion of hydrogen in various mixtures of nitrogen and oxygen, with special reference to the amount of nitrogen consumed and the quantities of ammonia and of nitrous and nitric acids produced. One of the experiments, chosen at random from the table given, had the following results: between 60 and 70 litres of hydrogen were burnt in 80 litres of a mixture containing 67·64 per cent. of oxygen and 32·36 per cent. of nitrogen, the total nitrogen transformed being 254·58 c.c. or 0·3182 gram. As the proportion of nitrogen to oxygen in the mixture is gradually increased, the quantity of nitrogen undergoing combustion rises to a maximum and then falls. Previous heating of the gases does not seem to have an appreciable effect on the proportion of nitrogen attacked, which is, however, increased by increasing the capacity of the combustion chamber. Using for the latter a flask of about 18 litres capacity, kept cool by means of water flowing over it and passing also a current of steam into the flask, 40 litres of hydrogen when burnt in 50 litres of a mixture containing 60 per cent. of oxygen and 40 per cent. of nitrogen, gave a yield of 456·12 c.c. of nitrogen entered into combination; this represents the greatest amount of transformation obtained in the author's experiments. Berthelot's experiments (Abstr., 1899, ii, 648; 1900, ii, 475, 476, 538) are referred to. T. H. P.

Action of Alkali Hydroxides and Alkaline Earths on Arsenic Pentasulphide. By LE ROY W. MCCAY (*Zeit. anorg. Chem.*, 1900, 25, 459—467).—The author has repeated his work on the preparation of thioxyarsenic acids (Abstr., 1899, ii, 745) in consequence of a statement by Weinland and Lehmann (*Chem. Zeit.*, 1889, 23, 865) that monothioxyarsenates are not formed. The results confirm those previously obtained, namely, that when arsenic pentasulphide is dissolved in warm solutions of an alkali hydroxide, ammonia or calcium, strontium or barium hydroxides, monothioxyarsenates and dithioxyarsenates are formed, of which the monothioxyarsenate predominates. E. C. R.

Density of Carbon Dioxide in the Solid and Liquid State. By U. BEHN (*Ann. Phys.*, 1900, [iv], 3, 733—743).—By means of suspension in ether, the density of solid carbon dioxide at -79° and under the pressure of 1 atmosphere is found to be 1·53. The density of the liquid under the pressure of its saturated vapour between $+25^{\circ}$ and -57° has been determined by a float method, allowance being made

for the contraction of the float at the high pressures. The following are the values obtained :

| Temperature. | Density. | Temperature. | Density. |
|--------------|----------|--------------|----------|
| 24.3° | 0.7202 | - 14.7° | 1.0051 |
| 22.4 | 0.7395 | - 26.9 | 1.0626 |
| 19.7 | 0.7740 | - 37.4 | 1.1054 |
| 16.4 | 0.8061 | - 48.6 | 1.1503 |
| 9.3 | 0.8661 | - 57.5 | 1.1809 |
| 0.1 | 0.9255 | | |

The results obtained agree well with those of Amagat (Abstr., 1892, 934), so far as the range of temperature is the same. J. C. P.

Electrolytic Preparation of Alkali Metals from fused Alkali Chlorides. By ARTHUR FISCHER (*Zeit. Elektrochem.*, 1900, 7, 349—354).—The author's experiments were made with a mixture of potassium and sodium chlorides in molecular proportion, from which sodium containing about 1 per cent. of potassium is obtained by electrolysis. The anode was of carbon, the cathode of iron, and the cathodic current density 5 to 10 amperes per sq. cm., the salt being fused by the current itself. The chief source of loss of sodium was found in the circulation set up in the liquid by the evolution of chlorine at the anode. The flow of liquid thus produced carries globules of metal away from the cathode towards the anode, where it recombines with chlorine. After many unsuccessful attempts, this source of loss was almost entirely eliminated by interposing a partition, dipping a little below the surface of the bath, between the electrodes. The partition consisted of a water-cooled iron tube of rectangular section covered externally by plates of marble.

T. E.

Solubility of Alkali Chlorides and Chlorates. By F. WINTERER (*Zeit. Elektrochem.*, 1900, 7, 360—362).—Tables are given of the solubility of (1) potassium chloride in solutions of potassium hydroxide, (2) sodium chloride in solutions of sodium hydroxide, (3) sodium chlorate in solutions of sodium chloride, and (4) potassium chlorate in solutions of potassium chloride, all at 20°. The specific gravities of the solutions are also included.

T. E.

Properties of Sodium Peroxide. By GEORGE F. JAUBERT (*Compt. rend.*, 1901, 132, 35—36).—Sodium peroxide prepared by the action of oxygen on the metal is yellow and not white, and the colour deepens on heating. It becomes very dark when heated to a high temperature in contact with silver, but the metal is attacked. Commercial samples of the peroxide which are white owe the absence of colour to the presence of a considerable proportion of the hydroxide and carbonate. Contrary to the usual statements, pure sodium peroxide does not deliquesce even after prolonged exposure to the air; it changes from yellow to white owing to its conversion into carbonate. If, however, the peroxide is exposed to air freed from carbon dioxide, the results are different and will be described subsequently.

C. H. B

Combination of Silver and Oxygen. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 131, 1159—1167).—Pure silver foil, when heated at 500—550° in sealed tubes containing dry oxygen, is disintegrated and partly converted into a yellowish-white powder giving the reactions of argentous oxide, Ag_2O , which seems to consist of a mixture of this compound with the finely divided metal. Comparable experiments made with dry air gave similar results. When moist oxygen or air is employed, the disintegration of the metal is more pronounced and the absorption of gas is greater. There is an appreciable action at 200°, but no alteration of the metal is observed at 100°. No disintegration occurs when the metal is heated at 550° with nitrogen, steam, or carbon dioxide. G. T. M.

Carbon Monoxide and Silver. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 131, 1167—1169. Compare preceding abstract).—Pure silver foil, when heated for 4 hours at 500° in a sealed tube containing dry carbon monoxide, is found to have withdrawn a considerable amount of carbon from this oxide, whilst an analysis of the gaseous residue indicates a diminution in the volume of gas and a production of 3.6 per cent. of carbon dioxide. This reaction begins even at 300°, but at this temperature its progress is very slow. Carbon monoxide, when heated at temperatures not exceeding 550°, yields carbon dioxide without depositing carbon; it is therefore probable that the deposition of carbon in the foregoing experiment results from the decomposition of a silver carbonyl compound analogous to the corresponding iron derivative. G. T. M.

Hydrogen and Silver. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 131, 1169—1170. Compare preceding abstracts).—Silver, when heated for 5 hours at 500—550° in sealed tubes containing hydrogen, shows signs of disintegration, which are, however, less pronounced than when produced by heating the metal in oxygen or carbon monoxide. The metal is permeable by gases at a red heat, for on heating a silver crucible containing sodium hydrogen carbonate over a gas flame at a temperature below the fusing point of sodium carbonate, it is found that, after 20 to 30 operations, the crucible has become charged with sodium and is very brittle. The presence of the alkali metal in the substance of the crucible is due to the reduction of the carbonate by the gases, particularly hydrogen and carbon monoxide, arising from the gas flame. G. T. M.

Calcium Amalgam. By JOHANN SCHURGER (*Zeit. anorg. Chem.*, 1900, 25, 425—429).—Calcium amalgam, CaHg_5 , obtained by heating a mixture of calcium with mercury in an atmosphere of carbon dioxide at 200—220°, crystallises in rhombic prisms or needles. It is a reducing agent, is unaltered at the ordinary temperature by dry hydrogen, nitrogen, or nitrous oxide, and oxidises slowly in dry air but very quickly in moist air. When heated with dry ammonia at the boiling point of mercury, it is converted into a mixture of calcium hydride and nitride, which decomposes violently in contact with water, with evolution of hydrogen and ammonia. When heated with nitrous oxide, it is converted into calcium oxide without the formation of nitride or

nitrosyl calcium. When heated with phosphine, it yields calcium phosphide and a yellow sublimate of mercury phosphide.

E. C. R.

Calcium Carbide and Silicon Carbide as Reducing Agents for Metallic Oxides, Salts, and Ores. By B. NEUMANN (*Chem. Zeit.*, 1900, 24, 1013—1014).—Chlorides are most easily reduced by calcium carbide; they must be quite dry, and are mixed with oxide, so that the reaction is $M_2O + 2MCl + CaC_2 = 6M + CaCl_2 + 2CO$ [$M = a$ metal]. Sodium chloride, or, better, a mixture of sodium and potassium chlorides, may be added as a flux. Copper, lead, and nickel can be obtained in a button; some metals remain in small scattered globules, and others volatilise to a large extent.

Sulphates, mixed with oxides, can be reduced according to the equation $M_2SO_4 + 2M_2O + CaC_2 = 6M + CaSO_4 + 2CO$; in the absence of oxide, a sulphide is formed. Carbonates are reduced according to the equation $M_2CO_3 + 2M_2O + CaC_2 = 6M + CaCO_3 + 2CO$. Oxides and roasted ores can be reduced in many cases, not in others; the reaction is $3M_2O + CaC_2 = CaO + 6M + 2CO$.

The reduction was effected in a clay crucible, which was heated in a gas furnace. The method is too expensive to find general application on the manufacturing scale; in the case of the rarer metals, where its cost is of less importance, the aluminium method is preferable, as it is neater, and requires no external heat.

Carborundum (silicon carbide) also reduces metallic oxides; sodium carbonate must be added as a flux.

C. F. B.

Reduction by means of Calcium Carbide. By FR. von KÜGELGEN (*Chem. Zeit.*, 1900, 24, 1060—1061. Compare Neumann, preceding abstract).—When calcium carbide is heated with a chloride in the absence of an oxide, the reaction is $2MCl + CaC_2 = 2M + CaCl_2 + 2C$, and the reduced metal does not fuse to a single button. A mixture of chloride and oxide, or an oxide alone, is not reduced according to the equations given by Neumann; the reactions are really $4M_2O + 2MCl + CaC_2 = 10M + CaCl_2 + 2CO_2$; $5M_2O + CaC_2 = CaO + 10M + 2CO_2$, the gas evolved being almost entirely carbon dioxide.

C. F. B.

Electrolysis of Calcium Chloride with Reference to the Formation of Chlorate. By SAMUEL A. TUCKER and HERBERT R. MOODY (*J. Soc. Chem. Ind.*, 1900, 19, 977—981).—The electrolysis of aqueous calcium chloride gives rise to a mixture of calcium chlorate and hypochlorite in proportions depending on the conditions; details are given of a large number of experiments made to determine the conditions most favourable to the formation of chlorate, with a view to utilising practically the waste calcium chloride of the ammonia soda process. The best concentration appears to be approximately 20 per cent., with horizontal platinum electrodes separated by 10 cm.; platinum is the only metal capable of withstanding the action. The electrodes should be of the same size, with a current density of 8 amperes per sq. decimetre; the best temperature is 80°. The

addition of sodium dichromate or hydroxide is advantageous under certain specified conditions. After the electrolysis has proceeded for about 14 hours, there is an appreciable drop in the efficiency, but this is not so great as to seriously interfere with the working value of the process, the efficiency after the 49th hour being about 76 per cent.

W. A. D.

Radioactive Substances. By FRITZ GIESEL (*Ber.*, 1900, 33, 3569—3671. Compare this vol., ii, 19).—The mother liquor from the recrystallisation of 2 kilos. of radium-barium chloride, after removing the greater portion of the lead and practically the whole of the radium, yields a precipitate with ammonia which is strongly radioactive, the activity of the insoluble oxalates of the rare earths subsequently obtained from the filtrate being quite small in comparison. The active precipitate, when dissolved in hydrochloric acid and subjected to the action of hydrogen sulphide, furnishes a sulphide which is yellow at first and then turns brown, the total product weighing 3 mg. and being as strongly radio-active as highly concentrated radium preparations. The rays emitted by the sulphide resemble those of polonium, readily undergoing absorption, and behaving similarly in the magnetic field. After one month, the preparation showed no diminution in radio-activity; it does not contain bismuth, but yields an insoluble sulphate, probably the lead salt, which is, however, far less active than the product subsequently obtained by precipitation with ammonia; the residue left on evaporating the final filtrate is also decidedly active. The radio-activity of these active fractions does not equal that of the original sulphide.

Röntgen rays and those emitted by radium are similar in their physiological action. About 0.2 gram of radium-barium chloride contained in a celluloid capsule, and applied for 2 hours to the inner side of the arm, produced a slight irritation which after 3 weeks developed into acute inflammation followed by desquamation and recovery of the affected part. The leaves of plants, when submitted to the rays, lose their chlorophyll and fade; paper when similarly treated becomes brown and friable.

G. T. M.

Plumbic Sulphate. By KARL ELBS and F. FISCHER (*Zeit. Elektrochem.*, 1900, 7, 343—347).—Plumbic sulphate is formed by electrolysis of sulphuric acid of sp. gr. 1.7 to 1.8 at temperatures not exceeding 30° with a current density at the anode of 0.02 to 0.06 amperes per sq. cm. The anode is of lead and should be immersed in a considerable volume of acid and separated from the cathode by a porous pot. The salt is partially deposited during the electrolysis in the form of a mud containing 60 to 85 per cent. of plumbic sulphate; a purer salt is afterwards deposited in indistinct crystals from the anode liquid.

Plumbic sulphate has a faint greenish-yellow shade, 100 c.c. of concentrated sulphuric acid dissolve about 0.345 gram of it at 30°; it reacts with or is insoluble in all ordinary solvents. Water decomposes it at once into sulphuric acid and lead peroxide. Sulphuric acid of sp. gr. less than 1.65 produces the same change more

or less quickly at the ordinary temperature. Concentrated hydrochloric and acetic acids dissolve it, forming lead tetrachloride and tetracetate. As an oxidising agent, it resembles but is more energetic than lead peroxide. With cold concentrated sodium hydroxide solution, a plumbate is formed.

Plumbic sulphate forms double salts with the sulphates of the alkali metals, ammonia, and the amines such as $K_2Pb(SO_4)_3$ and $(NH_4)_2Pb(SO_4)_3$. These are more stable than the single salt. They may be prepared by adding the finely powdered alkali sulphates to the solution of plumbic sulphate in concentrated sulphuric acid or by electrolysis (with lead anode) of sulphuric acid to which these salts have been added.

The ammonium and potassium salts are yellow, indistinctly crystalline powders, almost insoluble in sulphuric acid of sp. gr. 1.7; toward reagents, they behave like plumbic sulphate.

The formation of plumbic sulphate explains the rapid disintegration of the positive plates of accumulators when charged with too high currents. T. E.

Thallium Bromochlorides. By VICTOR THOMAS (*Compt. rend.*, 1900, 131, 1208—1211. Compare this vol., ii, 60).—The orange powder, obtained by adding to thallous chloride suspended in water sufficient bromine to convert it into a compound of the type Tl_2X_3 , dissolves in boiling water and its solution on cooling to 24° deposits a *bromochloride*, $Tl_4Cl_3Br_3$, crystallising in orange, hexagonal plates. A deposit of orange needles grouped in fern-like aggregates is produced on concentrating the solution but it is invariably contaminated with crystals of the preceding compound. The mother liquors on evaporation yield first a second crop of hexagonal plates and then a second crop of acicular crystals. These products all contain less bromine than the compound obtained in the first crystallisation. G. T. M.

Polysulphides of Copper. By ADELBERT RÖSSING (*Zeit. anorg. Chem.*, 1900, 25, 407—414).—*Copper hexasulphide*, Cu_2S_6 , is formed in very small quantity when copper salts are precipitated with yellow sodium sulphide solutions. It is easily prepared by fusing a mixture of anhydrous copper sulphate, sodium carbonate, and sulphur, dissolving the fused mass in cold water in an atmosphere of hydrogen, and precipitating the clear solution with hydrochloric acid; the orange-red precipitate is dried over sulphuric acid and extracted with carbon disulphide. All operations must be conducted at a low temperature and with the least possible exposure to the air. Copper hexasulphide dissolves in solutions of alkali or barium polysulphides, is decomposed into copper sulphide by colourless alkali sulphides, and is converted into the dark blue *sulphide*, Cu_4S_5 , when shaken with concentrated ammonia. The *trisulphide*, Cu_2S_3 , obtained by treating the hexasulphide in a reflux apparatus with boiling ether or carbon disulphide, is a dark brown, amorphous powder, more stable than the hexasulphide, and is converted into cupric sulphide when boiled with alcohol. E. C. R.

Copper Selenides. By HENRI FONZES-DIACON (*Compt. rend.*, 1900, 131, 1206—1208).—Cupric selenide, $CuSe$, formerly prepared

by Berzelius, is obtained in bluish-black, prismatic needles by heating cupric chloride at 200° in a stream of hydrogen selenide; at higher temperatures, the product fuses and begins to decompose. Cuprous selenide, Cu_2Se , is produced as an olive-green precipitate by the action of hydrogen selenide on a hydrochloric acid solution of cuprous chloride. This substance is obtained in lustrous octahedra and tetrahedra either by passing hydrogen selenide over the heated chlorides of copper or by reducing cupric selenide at a red heat in a current of hydrogen. Copper selenite, when reduced by hydrogen at high temperatures, yields only metallic copper, but crystals of cuprous selenide are produced when the salt is heated with carbon.

The selenides are decomposed by hydrogen chloride either in solution or at high temperatures, in the former case, hydrogen selenide being evolved; they are readily attacked by chlorine, oxidised to cupric selenite by nitric acid and dissolved by sulphuric acid with the evolution of sulphur dioxide. Ammonia attacks the cuprous selenide rather more readily than the cupric compound, whilst both substances are partially soluble in ammonium hydrosulphide. G. T. M.

Alleged Volatility of Mercurous Chloride at 37° . Reduction of Mercurous Compounds by Animal Tissues. By MARCO SOAVE (*Chem. Centr.*, 1900, ii, 1147—1148; from *Giorn. Farm. Chim.*, 1900, 50, 433—439).—The author has been unable to confirm Piccardi's observation that when powdered calomel, calomel ointment, or calomel suspended in water is heated at 37° , mercury vapour is evolved. Mercurous chloride and other mercurous compounds are decomposed, however, by the action of the gastric juice, intestinal fluids, the liver, kidneys, or blood, muscular tissue or proteids, with formation of mercury vapour. E. W. W.

Solubility of Mercury Haloid Salts, and especially of Mercuric Iodide, in Organic Solvents. By OTTOKAR ŠULC (*Zeit. anorg. Chem.*, 1900, 25, 399—404).—The solubilities of mercuric chloride, bromide, and cyanide and of mercurous chloride at 18 — 20° in chloroform, tetrachloromethane, bromoform, ethyl bromide, and ethylene dibromide are given, as are those of mercuric iodide in chloroform, tetrachloromethane, ethylene dichloride, *isobutyl* chloride, ethyl bromide, methyl, ethyl, *isopropyl* or *isobutyl* alcohol, methyl or ethyl formate, methyl or ethyl acetate, ether, acetone, acetal, chloral, epichlorhydrin, hexane, and benzene. Of these solvents for the iodide, methyl alcohol (6.512 in 100) is the best and hexane (0.072 in 100) the worst. The solutions of the iodide are yellow except in the case of ethyl bromide; the crystals which separate from them are either yellow or red, and all become red on standing (Kastle and Clark, *Abstr.*, 1900, ii, 141). The red colour of the solutions in ethyl bromide and bromoform is due to the liberation of iodine, which does not take place in the dark. Lead iodide is slightly decomposed in a similar manner when dissolved in ethyl bromide.

E. C. R.

Double Compounds of Mercuric and Potassium Iodides. By WLADIMIR PAWLOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 732—741).—A solution of mercuric iodide in aqueous potassium iodide

containing the salts in molecular proportion deposits hygroscopic, acicular crystals of the composition $\text{HgI}_2 \cdot \text{KI} \cdot \text{H}_2\text{O}$, which are soluble in alcohol without change, but are decomposed by water. The crystals melt at about 105° , and at 116.5° are completely decomposed with formation of a deep red liquid which boils at $191\text{--}193^\circ$.

If the two salts are present in the aqueous solution in the ratio $\text{HgI}_2 : 2\text{KI}$, the crystals obtained have the composition $\text{HgI}_2 \cdot 2\text{KI} \cdot 2\text{H}_2\text{O}$; at high temperatures, these decompose into potassium iodide and the double salt, $\text{HgI}_2 \cdot \text{KI}$.

T. H. P.

Cerium. By G. P. DROSSBACH (*Ber.*, 1900, **33**, 3506—3508).—Commercial cerium carbonate was partially purified and then converted into the double nitrate, $\text{Ce}_2(\text{NO}_3)_6 \cdot 3\text{NH}_4\text{NO}_3 \cdot 10\text{H}_2\text{O}$; this salt was fractionally crystallised some 200 times, but all fractions appear to be identical in every respect with the preparations obtained by older methods. The dioxide which is formed on ignition always has a pale yellow colour.

The double nitrate and also the compound $\text{Ce}_2(\text{NO}_3)_6 \cdot x\text{NH}_4\text{NO}_3 + \text{aq}$ are only slightly hygroscopic; they crystallise well, and any didymium salts are left in the mother liquors. Salts of lanthanum and the yttrite earths are somewhat more difficult to remove, but, after three crystallisations can be proved to be absent.

All metals of the cerium and yttrium groups dissolve readily in alkali carbonate solutions.

J. J. S.

Spectra of Samarium and Gadolinium. By EUGÈNE DEMARÇAY (*Compt. rend.*, 1900, **131**, 995—998).—The spectra of samarium and gadolinium previously described by the author (*Abstr.*, 1900, 597, 656) differ considerably from those described by Exner (*Sitz. Acad. Wiss. Wien*, 1900, **19**), and although the actual measurements of the latter are probably more accurate, yet many of the lines are wrongly identified. This is due to the fact that the specimens were impure, and Exner attributed to samarium all lines which were strong in the samarium spectrum and weak in the gadolinium, and *vice versa*. This negative evidence leads to errors; to obtain more certain results, the author has repeatedly purified his specimens, and observed the variation of the lines with each increase of purity, only those being attributed to samarium which remain of constant intensity; the wave-lengths of these with their relative intensities are given.

L. M. J.

Position of Indium in the Classification of the Elements. By CAMILLE CHABRIÉ and ÉTIENNE RENGADÉ (*Compt. rend.*, 1900, **131**, 1300—1303. Compare *Abstr.*, 1873, 846).—*Cæsium indium sulphate*, $\text{Cs}_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, was prepared by mixing hot concentrated solutions of the sulphates of the two metals, and on cooling separated in crystals belonging to the cubic system. One hundred parts of water at 16.5° dissolve 3.04 grams of the salt. Its aqueous solutions are acid to litmus and deposit a precipitate on heating. *Rubidium indium sulphate*, $\text{Rb}_2\text{SO}_4 \cdot \text{In}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, was prepared in a similar manner and crystallises in transparent octahedra. The existence of these two double sulphates of indium and also of its corresponding ammonium compound, and the fact that its hydroxide is soluble in

alkalis, point to indium being more allied in properties to aluminium than to iron.

Indiumacetylacetone, $\text{In}_2(\text{CHAc}_2)_6$, prepared by the action of acetylacetone on indium oxide, crystallises in flat, hexagonal prisms, melts at 183° , and sublimes and decomposes at $260\text{--}280^\circ$; it is insoluble in boiling water or cold alcohol, but dissolves readily in boiling alcohol.

H. R. LE S.

Hexahydrate of the Double Iodide of Manganese and Mercury. By D. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 742—744).—A saturated solution of mercuric iodide in saturated aqueous manganous iodide deposits yellowish, prismatic crystals of the composition $\text{MnI}_2 \cdot 2\text{HgI}_2 \cdot 6\text{H}_2\text{O}$, which when heated melt in their water of crystallisation and at higher temperatures decompose completely, leaving a residue of trimanganic tetroxide.

T. H. P.

Soluble Alkali Salts of Ferric Oxide and of Ferric Acid. By FRITZ HABER [and in part WALDEMAR PICK] (*Zeit. Elektrochem.*, 1900, 7, 215—221).—Poggendorf has stated that an anode of cast iron, in a concentrated solution of potassium hydroxide is oxidised to sodium ferrate; with other kinds of iron, this is not the case. The authors find that, immediately after closing the electric circuit, all varieties of iron are oxidised to ferrate and that the action is continuous provided that the solution of alkali hydroxide is concentrated and the current density low (about 0.001 ampere per sq. cm.). Under similar conditions, the yield of ferrate is greatest with cast iron and smallest with wrought iron; it is also greater with sodium than with potassium hydroxide, probably on account of the greater solubility of sodium ferrate. The quantity of ferrate reduced at the cathode (a platinum wire) in a cell without a diaphragm is comparatively trifling. The yield of ferrate depends on the temperature; under the same conditions, traces only of ferrate were formed at 0° , whilst at 70° the current efficiency was almost 100 per cent.

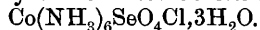
When the ferrate solution is boiled for a sufficiently long time, it becomes colourless or pale yellow, provided that care has been taken to use materials which are free from manganese. The yellowish solution contains a soluble ferrite and when kept deposits colourless crystals of a compound which very quickly decomposes when it is removed from the strongly alkaline liquid. The same solution of ferric oxide is obtained by boiling ferric hydroxide with a concentrated solution of sodium hydroxide. Addition of an alkaline sulphide gives a red coloration, due to the formation of the double alkali iron sulphide to which the "red liquors" of the Leblanc alkali manufacture owe their colour.

When pure iron is boiled gently for a few minutes with concentrated sodium hydroxide solution, the liquid is found to contain ferrous oxide. When exposed to air, this solution readily oxidises, to the ferric oxide solution. Both the solutions of ferrous and ferric oxide are readily oxidised to ferrate by electrolytic oxygen.

T. E.

Crystalline Form of Luteocobaltic Chlorosulphate and Chloroselenate. By TIMOTHÉE KLOBB (*Compt. rend.*, 1900, 131, 1305—1308).—Luteocobaltic chlorosulphate, $\text{Co}(\text{NH}_3)_6\text{SO}_4\text{Cl} \cdot 3\text{H}_2\text{O}$,

crystallises in prisms belonging to the rhombic system; they are isomorphous with the crystals of luteocobaltic selenate,



Full crystallographic measurements of the crystals of both salts are given in the paper. H. R. LE S.

Solubility of Some Salts in Water. By RUDOLF DIETZ, ROBERT FUNK, J. VON WROCHEM, and FRANZ MYLIUS (*Wiss. Abhandl. phys.-tech. Reichsanstalt*, 1900, 3, 425—477, and in part *Ber.*, 1901, 33, 3686—3696).—The greater part of this work has already been published (see Mylius and Funk, *Abstr.*, 1897, ii, 316, 442; Dietz, *Abstr.*, 1899, ii, 221; Funk, *Abstr.*, 1899, ii, 209). The paper, however, describes also an investigation of sodium and calcium chromates.

Normal sodium chromate, Na_2CrO_4 , exists as decahydrate, tetrahydrate, and anhydrous salt, each form having its own characteristic solubility; whilst the solubility of the decahydrate increases rapidly with rising temperature, that of the anhydrous salt increases only very slightly, a behaviour analogous to that of the isomorphous sodium sulphate. The dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7\cdot 2\text{H}_2\text{O}$ is stable up to 83° , at which temperature it changes into the anhydrous salt. The existence of sodium trichromate, $\text{Na}_2\text{Cr}_3\text{O}_{10}$ (compare Stanley, *Abstr.*, 1887, 110), is confirmed, but the authors show that it crystallises with $1\text{H}_2\text{O}$; the saturated solution at 0° contains 80 per cent. of the salt. Sodium tetrachromate, $\text{Na}_2\text{Cr}_4\text{O}_{13}\cdot 4\text{H}_2\text{O}$, has been prepared; it is stable in aqueous solution up to 40° , about which temperature it decomposes into chromium trioxide and trichromate.

When a saturated sodium hydroxide solution is added to a concentrated solution of normal sodium chromate, rhombohedral, yellow crystals separate of the composition $\text{Na}_4\text{CrO}_5\cdot 13\text{H}_2\text{O}$ —tetrasodium chromate; these crystals are very deliquescent, take up carbon dioxide from the air, and melt about 50° ; they cannot be obtained below 0° .

The solubility has been determined, and the conditions of existence studied, of five different modifications of calcium chromate; these are (1) monoclinic dihydrate, $\text{CaCrO}_4\cdot 2\text{H}_2\text{O}$, (2) rhombic dihydrate, (3) monohydrate, $\text{CaCrO}_4\cdot \text{H}_2\text{O}$, (4) hemihydrate, $\text{CaCrO}_4\cdot \frac{1}{2}\text{H}_2\text{O}$, (5) anhydrous salt. A crystallographic investigation of the first two modifications is added. The monohydrate is characterised by the fact that its solubility falls rapidly with rising temperature, the saturated solution containing 11.5 per cent. of the salt at 0° , and 3.1 per cent. at 100° . The above five modifications all exist in solution within a certain range of temperature; thus, at 18° , five distinct saturated solutions of calcium chromate may be obtained. J. C. P.

Uranium Nitrate. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1900, 131, 1219—1220).—Uranium nitrate is insoluble in petroleum, the aromatic hydrocarbons, carbon disulphide, or glycerol; it dissolves in methyl, ethyl, propyl, *isobutyl*, or amyl alcohol and also in acetone, ether, ethyl acetate, or formic or acetic acid, but is only sparingly soluble in turpentine.

One part of the salt dried at 85° dissolves in 2 parts of distilled

water at 13—14°; the heat of dissolution of $\text{UO} \cdot \text{NO}_3 \cdot 3\text{H}_2\text{O}$ at 17—18° is 3·8 Cal.

The nitrate dissolves in lime-water, but the solution subsequently yields a yellow, flocculent deposit; it is insoluble in solutions of ammonia or the alkali hydroxides, but is readily soluble in mineral acids, whether dilute or concentrated.

G. T. M.

Uranium Nitrate. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1900, 131, 1303—1305).—Aqueous solutions of uranium nitrate are slowly decomposed by diffused sunlight; if the solutions are acidified with hydrochloric acid or acetic acid, they become extremely stable. Solutions of uranium nitrate in commercial methyl alcohol or ethyl alcohol are readily decomposed by diffused sunlight, a black uranium oxide being deposited. One part of uranium nitrate, dried at 90°, dissolves in 55 parts of methyl alcohol at 11—12·6°; 30 parts of ethyl alcohol (85°) at 12·9—13°; 65 parts of pure acetone at 11·9—12·2°, and in 5·6 parts of acetic acid of sp. gr. 1·035, at 14—14·5°.

Tables are given of the sp. gr. of solutions of uranium nitrate in commercial methyl alcohol and in acetic acid.

H. R. LE S.

Production of Alloys of Tungsten and of Molybdenum in the Electric Furnace. By CHARLES L. SARGENT (*J. Amer. Chem. Soc.*, 1900, 22, 783—791).—The author has prepared small specimens of alloys of both tungsten and molybdenum with other metals, by heating a suitable mixture of the oxides of the desired metals with sugar carbon in the electric furnace in a carbon crucible, sometimes with a magnesia lining. By operating on 5 to 10 grams of mixture of oxides and carbon with a current of 70 to 90 volts, and 100 to 150 amperes, the operation was finished within 1 to 5 minutes.

Whilst tungsten and bismuth did not yield an alloy, definite results were obtained with molybdenum and bismuth. Copper alloyed with tungsten, but it refused to do so with molybdenum. Both tungsten and molybdenum failed to alloy with tin, and whilst the former failed to combine with manganese, the latter readily united with it. Both metals seemed to alloy with the greatest ease with cobalt, chromium, and nickel; these alloys may, perhaps, prove to be technically important, if readily obtainable in large quantities.

L. DE K.

A New Tungsten Phosphide. By ED. DEFACQZ (*Compt. rend.*, 1901, 132, 32—35).—When tungsten diphosphide is heated with copper in the electric furnace, it is decomposed; but if it is heated with a large excess of copper phosphide in a graphite crucible in a wind furnace and the product treated with dilute nitric acid, a new phosphide, WP, is obtained in grey, lustrous, prismatic crystals of sp. gr. 8·5. This *tungsten monophosphide* burns in air or oxygen at a red heat, and is likewise attacked by chlorine, but it is not decomposed by hydrofluoric or hydrochloric acid, or by hydrogen chloride. It is slowly oxidised by hot nitric acid, and is rapidly dissolved by a mixture of nitric and hydrofluoric acids, or by aqua regia. Sodium and potassium hydroxide solutions have no action on the phosphide, but the fused hydroxides and fused mixtures of alkali carbonates and nitrates readily

oxidised it, whilst fused potassium hydrogen sulphate attacks it slowly.

C. H. B.

Physico-chemical Researches on Tin. III. By ERNST COHEN (*Zeit. physikal. Chem.*, 1900, 35, 588—597. Compare Abstr., 1900, ii, 83, 212, 408).—The change of white tin into grey tin can be observed in filings of the metal, proving the incorrectness of the old view of Lewald, according to which the change took place only in block tin, and was probably due to a strained condition of the crystals. Mechanical vibration is found, so far, to be without influence on the transformation of white into grey tin. The presence of cobalt nitrate affects, not only the velocity of the transformation grey tin \rightleftharpoons white tin, but also the temperature of the maximum velocity. The velocity of the transformation is, further, very dependent on the history of the tin investigated, and consistent results can be obtained only with specimens which have been subject to the same conditions.

J. C. P.

Composition of Thorium Hydride and Nitride. By CAMILLE MATIGNON and MARCEL DELÉPINE (*Compt. rend.*, 1901, 132, 36—38).—The hydride obtained by the action of hydrogen on thorium at a dull red heat has the composition ThH_4 , and is readily dissociated at high temperatures.

The nitride obtained by heating thorium to redness in a current of nitrogen has the composition Th_3N_4 , and is slowly decomposed by cold water, but more rapidly on heating.

The hydride and the nitride burn in oxygen without incandescence.

C. H. B.

Hydrated Bismuth Oxide. By PAUL THIBAUT (*J. Pharm.*, 1900, [vi], 12, 559—561).—Bismuth oxide, prepared by the addition of an alkali to a solution of bismuth nitrate or chloride, always contains some basic nitrate or chloride. It may, however, be obtained free from these compounds by taking advantage of the fact that bismuth oxide is soluble in a solution of potassium hydroxide which contains glycerol.

Bismuth nitrate is intimately mixed with glycerol, water is added until the salt is entirely dissolved, and then potassium hydroxide until the precipitated oxide is redissolved. If dilute sulphuric acid is then added, a precipitate of bismuth oxide is produced, which is entirely free from any combined acid, and after drying in air, or in a vacuum over sulphuric acid, or at 100—105°, has the composition $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

H. R. LE S.

Soluble Bismuth Phosphate. By CLEMENTE MONTEMARTINI and U. EGIDI (*Gazzetta*, 1900, 30, ii, 421—446).—The preparation sold under the name of 'Bismuthum phosphoricum solubile' contains bismuth, sodium, and phosphoric acid, and is soluble in water. It is obtained by fusing together in certain proportions bismuth oxide, sodium hydroxide, and phosphoric acid. Its composition does not correspond with any formula representing the phosphorus present as either ortho-, meta-, or pyro-phosphoric acid, but agrees well with $\text{Bi}_5\text{Na}_{50}\text{P}_{39}\text{O}_{125} \cdot 3\text{H}_2\text{O}$. After precipitating and removing the bismuth from the solution as sulphide, the phosphorus is found to be present mostly as metaphos-

phoric acid, together with small quantities of the pyro-acid. In concentrated solution, the compound undergoes rapid hydrolytic dissociation, whilst with dilute solutions the change takes place slowly in the cold, but quickly on boiling; in all cases, a white precipitate is obtained, consisting of a mixture of bismuth oxide and phosphate containing the whole of the bismuth, the liquid at the same time acquiring an acid reaction and answering to the tests for meta- and pyro-phosphoric acids. On electrolysing an aqueous solution of the substance, bismuth is deposited on the anode, and a mixture of bismuth oxide and phosphate is precipitated. The depression of the freezing point of an aqueous solution shows that the compound is resolved into a number of ions, and, notwithstanding the precipitation of bismuth phosphate and oxide, the depression continuously increases; the electrical resistance, in a similar manner, shows a gradual decrease. From aqueous solutions alkalis precipitate mixtures of bismuth oxide and phosphate, whilst hydrochloric acid precipitates bismuth metaphosphate. On suspending the compound in ethyl or methyl alcohol and passing a current of hydrogen sulphide through the liquid, no precipitation of bismuth sulphide occurs, but this immediately takes place on adding water.

T. H. P.

Reduction of Nitroso-compounds of Ruthenium and Osmium. By LÉOPOLD BRIZARD (*Ann. Chim. Phys.*, 1900, [vii], 21, 311—383).—The paper contains a very detailed account of a study of ruthenium double salts, some of the results having been already published (*Abstr.*, 1899, ii, 559, 664).

Dihydorruthenium nitrosohydroxide, $\text{NO} \cdot \text{Ru}_2\text{H}_2(\text{OH})_3 \cdot 2\text{H}_2\text{O}$, produced either by the reduction of the nitrosohydroxide, $\text{NO} \cdot \text{Ru}(\text{OH})_3$, with an alkaline solution of formaldehyde or by the action of ammonia on potassium ruthenate, forms a gelatinous, dark-brown precipitate which on treatment with hydrochloric acid and potassium chloride yields the crystalline double chloride, $\text{NO} \cdot \text{R}_2\text{H}_2\text{Cl}_3 \cdot 3\text{KCl} \cdot 2\text{HCl}$; this salt is also obtained by the addition of potassium chloride to a solution of ruthenium nitrosochloride, $\text{NO} \cdot \text{RuCl}_3$, or the double nitrite, $\text{Ru}_2(\text{NO}_2)_6 \cdot 4\text{KNO}_2$, reduced by boiling with stannous chloride. Although stable at 360° , the double salt decomposes at higher temperatures with evolution of nitrogen, chlorine, hydrogen chloride, and water; it is reduced by hydrogen at a dull red heat, the volatile products being ammonium chloride, hydrogen chloride, and water, whilst the residue consists of ruthenium and potassium chloride.

The crystals of the double salt are very sparingly soluble in cold water, and when dissolved in this solvent the substance exists in a partially dissociated condition, the amount of dissociation increasing as the temperature rises. Chlorine passed into the freshly-prepared solution of the double chloride yields a precipitate of ruthenium tetroxide.

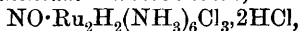
The *oxychloride*, $\text{NO} \cdot \text{Ru}_2\text{H}_2\text{Cl}_2 \cdot \text{OH} \cdot 2\text{H}_2\text{O}$, is precipitated by the addition of potassium hydroxide to the aqueous solution, whilst excess of this reagent produces the hydroxide $\text{NO} \cdot \text{Ru}_2\text{H}_2(\text{OH})_3 \cdot 2\text{H}_2\text{O}$.

The *double ammonium chloride*, $\text{NO} \cdot \text{Ru}_2\text{H}_2\text{Cl}_3 \cdot 2\text{HCl} \cdot 3\text{NH}_4\text{Cl}$, is produced on adding excess of ammonium chloride to the aqueous solution

of the corresponding potassium salt; the *silver* salt has a similar composition, $\text{NO} \cdot \text{Ru}_2\text{H}_2\text{Cl}_3, 2\text{HCl}, 3\text{AgCl}$.

Dihydroruthenium nitrosochloride, $\text{NO} \cdot \text{Ru}_2\text{H}_2\text{Cl}_3, 2\text{HCl}$, is an amorphous reddish-brown precipitate obtained on evaporating to dryness the hydrochloric acid solution of the corresponding oxychloride or hydroxide.

Ammoniodihydroruthenium nitrosochloride,



prepared by the action of ammonia on the preceding double chlorides, separates in orange-yellow crystals.

The double *salt*, $\text{NO} \cdot \text{Ru}_2\text{H}_2\text{Cl}_3, 2\text{HCl}, 3\text{KBr}$, produced by adding potassium bromide to a hydrochloric acid solution of dihydroruthenium nitrosochloride, separates in brown, anisotropic crystals sparingly soluble in water; it yields the oxychloride, $\text{NO} \cdot \text{Ru}_2\text{H}_2\text{Cl}_2 \cdot \text{OH}$, on treatment with potassium hydroxide.

The double *bromide*, $\text{NO} \cdot \text{Ru}_2\text{H}_2\text{Br}_3, 2\text{HBr}, 3\text{KBr}$, and the *ammonio-derivative*, $\text{NO} \cdot \text{Ru}_2\text{H}_2(\text{NH}_3)_6\text{Br}_3, 2\text{HBr}$, are obtained by methods similar to those employed for the chlorine derivatives; it was, however, found impossible to isolate the corresponding double iodides.

The double *silver nitrite*, $\text{Ru}_2\text{H}_2(\text{NO}_2)_4, 3\text{AgNO}_2, 2\text{H}_2\text{O}$, is a brownish-yellow precipitate produced by adding silver nitrate to a cold solution of the corresponding potassium salt (compare Abstr., 1899, ii, 664), on double decomposition with ammonium chloride, it yields the corresponding double *ammonium salt*, $\text{Ru}_2\text{H}_2(\text{NO}_2)_4, 3\text{NH}_4\text{NO}_2, 2\text{H}_2\text{O}$.

Potassium aminochloro-osmate, $\text{NH}_2 \cdot \text{OsCl}_2, 2\text{KCl}$, is a crystalline salt prepared by reducing potassium osmiate with stannous chloride; its *hydrochloride* has the composition indicated by the formula $\text{NH}_2 \cdot \text{OsCl}_3, 2\text{KCl}, \text{HCl}$. The solutions obtained by reducing the osmiate with formaldehyde or ferrous chloride do not yield crystallisable double salts.

G. T. M.

Mineralogical Chemistry.

Enrichment of Mineral Veins by Later Metallic Sulphides. By WALTER HARVEY WEED (*Bull. Geol. Soc. Amer.*, 1900, 11, 179—206).—Silver, copper, lead, &c., may be leached out as carbonates and sulphates from the upper gossan zone of mineral veins, and carried down by surface waters to be reduced again by sulphides of iron in the unaltered portions of the vein. Rich secondary deposits of sulphides may thus be formed in veins which are in other parts poor. These changes are discussed in detail, and suggestions are made as to the nature of the chemical reactions which may take place. L. J. S.

Mohawkite, Stibio-domeykite, Domeykite, Algodonite and some Artificial Copper Arsenides. By GEORGE A. KOENIG (*Amer. J. Sci.*, 1900, [iv], 10, 439—488).—General notes are given of the occurrence of copper arsenides in the Lake Superior copper mining

region, and two new ones are described under the names mohawkite and stibio-domeykite. *Mohawkite* from the Mohawk mine, Keweenaw Co., Michigan, is massive and very brittle; the colour is grey with a tinge of yellow, tarnishing easily to dull purple. Analysis I gives the formula $(\text{Cu}, \text{Ni}, \text{Co})_3\text{As}$; the mineral is therefore a nickeliferous domeykite (Cu_3As) . Domeykite from the Sheldon-Columbia mine gave II. Crystallised domeykite was produced by heating together copper and arsenic; the arsenide, Cu_2As , is also formed at the same time. *Stibio-domeykite* (anal. III), from the Mohawk mine, differs only from ordinary domeykite in containing a small percentage of antimony, amounting in one specimen to 1.29. Analysis IV (also CaCO_3 , 2.41; MgCO_3 , 0.60) is of an intimate mixture of mohawkite and whitneyite; as shown by other analyses, this mixture varies in composition. Algodonite, of a steel-grey colour, from the Pewabic mine gave V.

| | As. | Sb. | Cu. | Ni. | Co. | Fe. | Total. | Sp. gr. |
|------|-------|------|-------|------|------|-------|--------|---------|
| I. | 28.85 | — | 61.67 | 7.03 | 2.20 | trace | 99.75 | 8.07 |
| II. | 26.14 | — | 74.00 | 0.06 | | | 100.20 | 7.9486 |
| III. | 26.45 | 0.78 | 72.48 | 0.24 | | | 99.95 | 7.902 |
| IV. | 15.07 | — | 79.36 | 0.61 | 0.82 | 0.36 | 99.23 | — |
| V. | 16.08 | — | 83.72 | 0.08 | | | 99.88 | 8.383 |

L. J. S.

Tellurides from Colorado. By CHARLES PALACHE (*Amer. J. Sci.*, 1900, [iv], 10, 419—427).—Sylvanite has already been inferred to be present in the telluride ores of Cripple Creek (Abstr., 1896, ii, 612, 613), and recently crystals have been found in several of the mines. A detailed crystallographic description is given of this new material. The habit is tabular parallel to (010), or prismatic parallel to the zone [111, 010], and some crystals are twinned on (101). Sp. gr. 8.161. Analysis of crystals gives results agreeing with the sylvanite formula, AuAgTe_4 .

| Au. | Ag. | Te. | Fe. | Insol. | Total. |
|-------|-------|-------|------|--------|--------|
| 26.09 | 12.49 | 60.82 | 1.19 | 1.02 | 101.61 |

The goldschmidtite of Hobbs (Abstr., 1899, ii, 493) is shown to be crystallographically identical with sylvanite, the habit and twinning being the same as for the crystals now described. In an accompanying note, W. H. Hobbs admits this identity, and remarks on the untrustworthiness of his analysis, which had to be made on a very small sample.

Hessite crystals from Colorado are described; these, although cubic, are rhombohedral in habit.

L. J. S.

Opals from Tuscany. By GIOVANNI D'ACHIARDI (*Jahrb. Min.*, 1900, ii, 348—350; from *Atti Soc. Toscana Sci. Nat. Proc. Verb.*, 1899, 11, 114—136).—Determinations of the chemical and optical characters are given for seven varieties of opal from various localities in Tuscany. Analysis I is of grey, almost colourless, transparent opal occurring as nodules in serpentine at San Piero, Elba; thin sections are optically isotropic. II, Opaque, milk-white opal occurring with, and graduating into, the last; the porcellaneous appearance is due to enclosed air,

it is almost isotropic. III, Black opal, as pitch-like blocks at the contact of serpentine and granite from the same locality; it is in part feebly birefringent, and encloses bastite, iron oxides, zircon, and garnet. IV, Grey opal from Jano; this is a silicified serpentine, and is veined with chalcedony; it is almost isotropic. V, Red and grey opal occurring with serpentine at Impruneta. VI, Fiorite, from Santa Fiore, Monte Amiata, is of different origin from the above, and has been formed in water through which silicon fluoride has bubbled; it consists of alternate layers of isotropic opal and birefringent chalcedony. VII, Diatomaceous earth from Castel di Piano, Monte Amiata.

| | I. | II. | III. | IV. | V. | VI. | VII. |
|--------------------------------------|-------|-------|------------------|------------------|-------|------|-------|
| SiO ₂ | 89·55 | 86·54 | 82·11 | 87·62 | 83·13 | — | — |
| Al ₂ O ₃ | 0·49 | 1·73 | { 1·61 5·50 } | { 1·45 1·71 } | 3·43 | — | — |
| Fe ₂ O ₃ | | | | | | | |
| CaO | 0·63 | 0·55 | 1·57 | 0·36 | 0·81 | — | — |
| MgO | 0·57 | 0·74 | trace | 0·47 | 1·73 | — | — |
| H ₂ O { 80—90° ... | 1·02 | 5·68 | 5·50 | 4·90 | 4·18 | 0·22 | 5·98 |
| { 130—320° | 6·48 | 3·15 | 2·49 | 1·24 | 3·18 | 2·96 | 1·97 |
| at { red heat... | 0·53 | 0·57 | 1·09 | 0·60 | 1·87 | 2·29 | 3·57 |
| Total H ₂ O | 8·03 | 9·40 | 9·14 | 6·74 | 9·23 | 5·47 | 11·52 |
| | 99·27 | 98·96 | 99·93 | 98·35 | 98·33 | — | — |

Sp. gr. 1·99–2·03 1·94–1·97 2·065 — — — —

Curves are given showing the amounts of water given off at different temperatures for each of these opals. The total water present and the temperature at which it is lost, depends on the origin and the nature of the material; for those of primary origin (I and VI) little water is lost below 100°. No definite formula can be given for opal.

L. J. S.

Chromite from Kraubat, Upper Styria. By FRANZ RYBA (*Zeit. prakt. Geol.*, 1900, 337–341).—Here, as at other localities (*Abstr.*, 1899, ii, 494), chromite occurs as a concentrated primary constituent in olivine-rock, which is usually altered to serpentine. Analysis of the chromite by R. Vambera gave:

| | | | | | | |
|--------------------|------|---------|------|----------------------------------|----------------------------------|--------|
| SiO ₂ . | MgO. | CoO[?]. | FeO. | Al ₂ O ₃ . | Cr ₂ O ₃ . | Total. |
| 4·3 | 9·7 | 6·4 | 9·1 | 13·7 | 56·2 | 99·4 |

L. J. S.

Dolomite from Ceylon. By EMIL CHR. SCHIFFER (*Inaug.-Diss. München*, 1900, 32–45).—A coarsely crystalline dolomite occurring as a band in gneiss at Wattegama contains numerous mineral enclosures, of which the following analyses (in each case the mean of two or more) are given. Selected clear rhombohedra of dolomite gave the results under I; cleavage angle, 73°43'; sp. gr., 2·896. The rough material is shown by analysis II to be also normal dolomite:

| | CO ₂ . | CaO. | MgO. | Gangue. | Total. |
|-----|-------------------|-------|-------|---------|--------|
| I. | 47·72 | 30·45 | 21·87 | — | 100·04 |
| II. | 46·88 | 31·12 | 20·85 | 0·87 | 99·72 |

Rounded prismatic crystals of sky-blue apatite gave the results under III :

| | P ₂ O ₅ . | CaO. | FeO. | MgO. | Cl. | F. | H ₂ O. | Total less O for Cl,F). |
|------|---------------------------------|-------|------|------|------|------|-------------------|----------------------------|
| III. | 40·19 | 54·43 | 1·16 | 1·20 | 1·06 | 3·16 | Nil. | 99·63 |

Phlogopite as light brown, pyramidal crystals and scales with $2E=14^{\circ}23'$, gave IV. Hydrophlogopite occurs as globular and vermiform masses of a lighter colour than the phlogopite, with which it is often intergrown, and of which it is an alteration product ; analysis V shows it to differ from phlogopite in containing less alkalis and more water, and to differ from the vermiculites in containing more alkalis. Pale green serpentine, occurring as irregular and small globular masses, gave results (VI), indicating that it has been derived from forsterite. Snow-white serpentine gave VII, which agrees, like the last, with the formula, $H_6R_3Si_2O_{10}$.

| | SiO ₂ . | Al ₂ O ₃ . | CaO. | MgO. | Na ₂ O. | H ₂ O. | Total. |
|------|--------------------|----------------------------------|------|-------|--------------------|-------------------|--------|
| IV. | 39·71 | 15·48 | — | 28·53 | 8·99 | 5·59 | 98·30 |
| V. | 40·13 | 14·24 | — | 23·78 | 7·69 | 13·49 | 99·33 |
| VI. | 39·29 | 1·78 | 1·82 | 39·04 | — | 18·15 | 100·08 |
| VII. | 39·65 | 3·18 | 1·75 | 38·60 | — | 16·53 | 99·71 |

Pyrites occurs as crystals and grains, but is usually represented by limonite pseudomorphs. Analysis gave : Fe 44·99, S 53·79, gangue $1·22=100·00$.

Spinel and pyrrhotite are also present as enclosures in the dolomite.

L. J. S.

Minerals of Ceylon. By FR. GRÜNLING (*Zeit. Kryst. Min.*, 1900, 33, 209—239).—An account of a mineralogical expedition to Ceylon. Several analyses of minerals by E. C. Schiffer are given (compare preceding abstract).

L. J. S.

Influence of the Presence of Iron on the Change in State of Boracite. By FRIEDRICH RINNE (*Jahrb. Min.*, 1900, ii, 108—116).—Crystals of boracite which contain iron (up to 7·9 per cent. FeO) have a more or less pronounced greenish tint. With increase in temperature the colour gradually becomes deep bluish-green, but this change takes place before, and is not connected with, the change from the rhombic to the cubic modification of boracite. In boracite containing iron, the temperature at which the change in state takes place is sensibly higher (285°) than in colourless boracite (265°), and the change takes place less sharply. At 285° , the birefringence of iron-boracite becomes much weaker, the division into fields, as seen in polarised light, becomes different ; even at 400° , the material is not wholly isotropic. These optical anomalies, which are described in detail, are considered to be due to the isomorphous mixing of iron- and magnesium-boracite.

L. J. S.

Robellazite, a new Mineral. By E. CUMENGE (*Bull. Soc. franç. Min.*, 1900, 23, 17—18).—This was found in Colorado by M. Robellaz as small, black, concretionary masses associated with carnotite (Abstr., 1899, ii, 434 ; 1900, ii, 599). From qualitative tests, it appears to be

a niobate, tantalate, and tungstate of vanadium, with aluminium, iron, and manganese. L. J. S.

Apophyllite from Sulitelma. By ANDERS HENNIG (*Jahrb. Min.*, 1900, ii, Ref. 354—357; from *Geol. För. Förh.*, 1899, 21, 391—415).—Apophyllite from Mount Sulitelma, in northern Scandinavia, forms, with stilbite, a crust on pyritiferous quartz. The weathered crystals on the exterior are white and opaque, but the inner ones are colourless and transparent. Measurements are given of the numerous vicinal faces, which are more abundant on the cloudy, weathered crystals; these appear to be connected with a loss of water, since they may be artificially developed by simply heating the crystals. The optical examination shows the presence of a central portion of "chromocyclite" surrounded by leucocyclite, and the change in the optical characters observed on heating the isolated "chromocyclite" suggests that the latter has been derived from the former by the loss of about 2 per cent. of water. The following analysis of crystals, by L. Ramberg, gives the formula $\text{Ca}(\text{CaF}_2, \text{K}_n)\text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$. Numerous determinations are given of the loss of water, at different temperatures, of apophyllite from various localities:

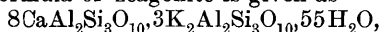
| SiO_2 . | $\text{Al}_2\text{O}_3(\text{Fe}_2\text{O}_3)$. | CaO . | K_2O . | Na_2O . | H_2O . | F. | Total. |
|------------------|--|----------------|------------------------|-------------------------|------------------------|------|--------|
| 52.61 | 2.23 | 23.82 | 4.96 | 0.05 | 15.67 | 1.24 | 100.58 |

L. J. S.

Zeagonite as a new Alteration Product of Nephelite. By STANISLAUS J. THUGUTT (*Bull. Internat. Acad. Sci. Cracow*, 1899, 168—169; and *Jahrb. Min.*, 1900, ii, 65—79).—Analysis I is of partially altered nephelite isolated by means of a heavy liquid from the nephelinite of Löbau, Saxony; II is of an alteration product, referred to zeagonite, of the nephelite. Other analyses of mixtures of these are given. The figures under III, which are assumed to represent the true composition of zeagonite, are calculated from II by deducting the residue insoluble in hydrochloric acid, 13.97 per cent. of nephelite (calculated from Na_2O , 1.93) and 4.43 per cent. of limonite (assuming the excess of the molecular ratio 1:1 of sesquioxides over other bases to be due to Fe_2O_3):

| | SiO_2 . | $\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$. | CaO . | MgO . | K_2O . | Na_2O . | Insol. | H_2O . | Total. |
|------|------------------|--|----------------|----------------|------------------------|-------------------------|--------|------------------------|--------|
| I. | 42.69 | 33.51 | 2.50 | 0.10 | 4.49 | 14.24 | 1.10 | 1.59 | 100.22 |
| II. | 38.97 | 26.03 | 7.47 | 0.25 | 4.60 | 1.93 | 3.01 | 16.80 | 99.06 |
| III. | 42.34 | 22.77 | — | 9.10 | 0.31 | 5.10 | — | 20.38 | 100.00 |

From III the formula of zeagonite is given as



to be in conformity with the author's constitutional formula for nephelite, namely, $8\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 4\text{Na}_2\text{Al}_2\text{O}_4 \cdot 3\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10}$ (*Abstr.*, 1895, ii, 358). As represented by these formulæ, the alteration from nephelite to zeagonite could be effected by water containing calcium salts. Zeagonite [= gismondite] usually occurs as crystals lining the cavities of rocks, but in the case here described it penetrates the whole rock as a pseudomorph after nephelite, the usual alteration products of which are natrolite, mica or cancrinite. L. J. S.

"Blue Asbestos" [Crocidolite]. By H. F. OLDS (*Trans. Inst. Mining and Metallurgy*, 1899; and *Eng. and Mining J.*, New York, 1899, 67, 528).—The crocidolite or "blue asbestos" of Griqualand West occurs as veins in dark brown shale. It is mined to a considerable extent for commercial purposes. The composition is:

| SiO ₂ . | FeO. | MgO. | Na ₂ O. | H ₂ O. | Total. |
|--------------------|------|------|--------------------|-------------------|--------|
| 51.1 | 35.8 | 2.3 | 6.9 | 3.9 | 100.0 |

L. J. S.

Minerals [Garnet] from the Fichtelgebirge. By ERNST DÜLL (*Jahrb. Min.*, 1900, ii, Ref. 357—359; from *Beil. z. Jahresb. k. Luitpold-Kreisrealschule in München*, 1899, 8, 47 pp.).—A description is given of the minerals from fragments of an albite-bearing phyllite-gneiss found near Schönbrunn in the Fichtelgebirge. These include secondary minerals present throughout the rock, and also minerals occurring in veins. A green garnet, in rhombic-dodecahedral crystals, is the most prominent; the following analysis proves this to be topazolite, and not grossularite as formerly supposed:

| SiO ₂ . | TiO ₂ . | Fe ₂ O ₃ . | Al ₂ O ₃ . | FeO. | CaO. | MnO. | MgO. | Total. |
|--------------------|--------------------|----------------------------------|----------------------------------|------|-------|-------|-------|--------|
| 36.65 | 0.40 | 18.48 | 9.07 | 0.82 | 34.04 | trace | trace | 99.46 |

L. J. S.

Chemical and Mineralogical Constituents of Keuper Marl. By ERNST ANTON WÜLFING (*Jahresb. Ver. vaterl. Naturk. Württemberg*, 1900, 56, 1—46).—An attempt is made to determine the mineralogical composition of red and green marls from the Keuper beds near Tübingen. Bulk analyses of the same samples have already been published (*Ber.*, 1899, 32, 2214). Under the microscope, minute grains of quartz, orthoclase, mica, rhombohedral carbonates, &c., may be recognised; and from analyses of the portions soluble in acids of various strengths and temperatures is inferred the presence of a chlorite having the composition $2\text{MgO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$, a clay of the composition $\text{Al}_2\text{O}_3, 4\text{SiO}_2, 2\text{H}_2\text{O}$, and some kaolin. The relative amounts of each of these constituents vary very considerably in the different samples. The name *geolyte* is proposed to replace the term "Bodenzeolith" used by agricultural chemists for those constituents of soils which are easily soluble and of undefinable mineralogical composition, but which have little in common with zeolites. L. J. S.

Carbonaceous Gneiss in the Black Forest. By HARRY ROSENBUSCH (*Mittel. Grossh. Badischen Geol. Landesanst.*, 1899, 4, 9—48).—The gneisses of the Black Forest have been derived from both sedimentary and igneous rocks. Those derived from sedimentary rocks often contain carbon in the form of small scales of graphite or as graphitoid. The latter, as a dull, very fine dust, impregnates the whole rock, but only surrounds, and is not included in, the mineral grains; it is probably of organic origin. The rock with graphitoid gives off ammonia when heated; it contains free carbon, 1.31, nitrogen, 0.081 per cent. The residue obtained on dissolving

the rock in hydrofluoric and sulphuric acids gave, on analysis by Mohr :

| C. | N. | H ₂ O. | Residue. | Total. |
|------|-----|-------------------|----------|--------|
| 77.4 | 1.2 | 3.5 | 16.1 | 98.2 |

L. J. S.

Average Composition of British Igneous Rocks. By ALFRED HARKER (*Geol. Mag.*, 1899, N.S. Dec. iv, 6, 220—222).—The mean of 397 published analyses of British igneous rocks is given under I; corrections have been made for TiO₂ and MnO, but not for Fe₂O₃ and FeO. The mean sp. gr. of 736 rocks is 2.763. With this is compared F. W. Clarke's mean (II) of 680 analyses of American rocks :

| | SiO ₂ . | TiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | MgO. |
|-----|--------------------|--------------------|----------------------------------|----------------------------------|------|------|------|
| I. | 58.46 | 0.69 | 15.13 | 5.34 | 2.40 | 0.40 | 3.84 |
| II. | 59.77 | 0.53 | 15.38 | 2.65 | 3.35 | 0.09 | 4.40 |

| | CaO. | Na ₂ O. | K ₂ O. | H ₂ O. | P ₂ O ₅ . | Total. |
|-----|------|--------------------|-------------------|-------------------|---------------------------------|--------|
| I. | 4.98 | 3.25 | 2.74 | 2.23 | 0.25 | 99.71 |
| II. | 4.81 | 3.61 | 2.83 | 1.51 | 0.21 | 99.14 |

Taking rocks from special districts, other mean values are obtained. The mean silica percentage of 96 rocks from the English Lake district is 58.75, and the mean sp. gr. of 113 is 2.737. Of 82 Malvern rocks the mean silica percentage is 54.81, and the mean sp. gr. of 38 is 2.841.

L. J. S.

Mud from the Salt Mines of Ischl. By E. WIENER (*Chem. Centr.*, 1900, ii, 1185; from *Wien.-klin. Woch.*, 1900, 13, 646—648).—Mud deposited in the salt mines at Ischl, in Salzburg, possesses therapeutic properties and consists of gypsum and clay with sodium chloride, &c. Analyses are given of the portions soluble in water and dilute acid.

L. J. S.

Salt Lakes of Roumania. By PAUL BUJOR (*Ann. Sci. Univ. Jassy*, 1900, 1, 149—186).—A list of the salt lakes of Roumania is given, and two of them are described in detail, with chemical analyses of the water and mud.

L. J. S.

Hot Springs of Gastein. By ERNST LUDWIG and THEODOR PANZER (*Tsch. Min. Mitth.*, 1900, 19, 470—488; and *Wien. klin. Woch.*, 1900, 13, 617—622).—Near Gastein in Salzburg there are 18 hot springs which issue from an intrusive mass of granite-gneiss. The temperature varies from 24.4° to 49.4° in the different springs. An analysis is given of water from the Elizabeth spring of which the temperature is 49.1°; sp. gr. 1.000367. The results obtained agree closely with those of earlier analyses made at various times since 1828.

L. J. S.

Composition of a Sulphated Calcareous Water at Lautaret (Hautes-Alpes). By JOSEPH A. MULLER (*Bull. Soc. Chim.*, 1900, [iii], 23, 910—912).—The temperature of this water is sensibly constant at about 25.3°. It yields a solid residue of 5.216 grams per kilogram, consisting chiefly of sodium chloride, calcium carbonate, and calcium, magnesium and sodium sulphates.

N. L.

Physiological Chemistry.

The influence of Sterilised Air on Animals. By J. J. KIJANITZIN (*Virchow's Archiv*, 1900, 162, 515—533).—The experiments were made on rabbits, and the apparatus used for supplying them with sterilised air is described and figured. Under these circumstances, the metabolic functions are reduced, and the animals waste. This is considered to support the author's previous contention, that the micro-organisms of the atmosphere play a useful part in metabolism. Their special function is considered to be to provide the blood with oxidising ferments, as in their absence the oxidation changes in the organism are diminished, and this leads to an accumulation of intermediate waste products of metabolism (leucomaines).
W. D. H.

Metabolism of Creatinine. By J. J. R. MACLEOD (*Proc. Physiol. Soc.*, 1900, vii—viii).—The creatinine excreted in the urine may be divided into an endogenous portion arising during metabolism, and an exogenous portion from the creatine and creatinine of the food. In order to investigate the first of these, a diet must be taken free from creatine and creatinine. The experiments indicate that urea does not arise from creatinine. In cases of muscular atrophy, no diminution was noted. In cases of splenic enlargement, the creatinine excreted was only half the normal amount. It is probable that the spleen exercises some control over creatinine metabolism. The number of leucocytes in the blood does not influence the amount excreted. Further experiments are in progress.
W. D. H.

Metabolism of Hippuric Acid. By ADOLF JÖLLES (*Pflüger's Archiv*, 1900, 82, 553—558).—On the administration of hippuric acid, all the nitrogen appears as urea. It is regarded as probable that in the oxidation processes of proteids in the body, of which the final product is urea, glycine and other amino-acids are in part formed, which are ultimately oxidised to form urea.
W. D. H.

Metabolism in Cephalopods. By OTTO VON FÜRTH (*Zeit. physiol. Chem.*, 1900, 31, 353—380).—A historical review of this subject is followed by a description of the method adopted of collecting large quantities of urine from the octopus. A sediment found in some cases contains uric acid. The fluid contains ammonia, but no urea; a number of other products of nitrogenous katabolism were also sought for, but in the main with negative results. The most striking fact is the presence of proteid; albuminuria appears to be in these animals a physiological process.
W. D. H.

Estimation of Rennet-ferment in Gastric Juice. By LÉON MEUNIER (*J. Pharm.*, 1900, [vi], 12, 457—465).—The amount of rennet-ferment in gastric juice is estimated by the time required for a known volume of the gastric juice to produce coagulation in a milk which is kept at 40—41°, and to which a small quantity of calcium chloride has been added. The strength of the gastric juice in rennet-

ferment is defined as the amount of milk coagulated by unit volume of the gastric juice in 10 minutes and under the conditions of experiment described in the paper. A standard milk was used for all the experiments and was prepared as follows. Several samples of fresh milk were mixed together, boiled, and filtered from the precipitated albumin. The filtrate was then boiled and when boiling was poured into small flasks which were then corked, and heated at 115° for 10 minutes. The following conclusions were arrived at: (1) Rennet-ferment keeps very well in the gastric juice. (2) The secretion of rennet-ferment in adults reaches its maximum one hour after the partaking of a meal consisting of bread and tea, and remains at a maximum until the end of the digestive period. (3) In normal cases, the "strength in rennet-ferment" varies between 500 and 2000. (4) In pathological cases, a diminution in the amount of rennet-ferment gives valuable information as to the condition of the glandular structure of the membrane of the stomach.

H. R. LE S.

Alkalinity of the Blood. By WALDVOGEL (*Chem. Centr.*, 1900, ii, 1156; from *Deutsch. med. Zeit.*, 28, 685—686).—A number of estimations of the alkalinity of the blood were performed by a modification of the Salkowski-Schlösing method. The alkalinity is lessened in typhoid fever, but there is no parallelism between rise of temperature and fall of alkalinity.

W. D. H.

Glycolytic Decomposition of Sugars. By P. PORTIER (*Compt. rend.*, 1900, 131, 1217—1218).—When blood is collected and preserved under aseptic conditions, the amount of dextrose which it contains rapidly diminishes, the rate of disappearance of this sugar varying with the temperature.

It is found that small quantities (0.2 per cent.) of galactose, levulose, and maltose are similarly decomposed when added to the blood of the dog or rabbit, whilst sucrose, lactose, and xylose remain unaltered.

G. T. M.

Effect of Intravenous Injection of Milk on the Coagulability of the Blood. By L. CAMUS (*Compt. rend.*, 1900, 131, 1309—1312).—If cow's milk is freed from cream by the centrifuge and injected intravenously into dogs, the blood of the latter animals is rendered incoagulable. The substance to which this is due has not been determined, but it is not a lysin, as boiling does not affect the action. Dog's milk injected into dogs has the same effect. Dogs differ somewhat in their reaction to the injection, and this probably accounts for Delezenne's statement that dogs are refractory in this particular to dogs' milk. Delezenne's suggestion that this refractiveness is most marked in dogs during the lactation period has not yet been experimentally tested.

W. D. H.

Osmosis in Marine Invertebrates. By R. QUINTON (*Compt. rend.*, 1900, 131, 905—908, 952—955).—The experiments recorded do little more than confirm what Fredericq found in 1882 (*Bull. Acad. Roy. Belg.*, 4, 209), namely, that in many marine forms the salts in the hæmolymp are the same as those in the sea. The outer membrane of these animals simply plays the part of a membrane as in physical osmosis.

W. D. H.

Muscular Serum. By CHARLES RICHET (*Compt. rend.*, 1900, 131, 1314—1316).—The term muscular serum is applied to the richly albuminous fluid which can be expressed from flesh that has undergone rigor. It has the following percentage composition (from beef):

| | |
|---|------|
| Dry residue | 6.71 |
| Ash | 0.89 |
| Total nitrogen | 1.05 |
| Nitrogen from proteids | 0.8 |
| Nitrogen from substances soluble in hot alcohol.. | 0.25 |

Of the mineral matters, potassium phosphate is the most abundant. The serum contains small quantities of sugar, hæmoglobin, and myohæmatin (?). Injected under the skin or into a vein, 5 c.c. per kilo. of body weight produces a fall of blood pressure, stupor, and death in from 24—48 hours; 3 c.c. produce the same effects more slowly. The blood is coagulable. Abdominal congestion is the most marked appearance *post mortem*. Boiling destroys the toxic properties. Given by the mouth, the serum is harmless, and is even stated to cure inoculated tuberculosis in dogs.

W. D. H.

Proteids of Invertebrate Muscle. By OTTO VON FÜRTH (*Zeit. physiol. Chem.*, 1900, 31, 338—352).—It is possible to obtain from the muscles of invertebrate animals a muscle plasma which coagulates spontaneously. Most of the experiments recorded were performed with the muscles of cephalopods (octopus and sepia), but holothurian muscle gave also corresponding results. The proteids separated out differ in various points (coagulation temperature, precipitability by salts, &c.) from the myogen and myosin previously described by the author in mammalian muscle.

The paper concludes with a discussion of the dependence of heat rigor on the heat coagulation temperature of the proteids in muscle. No reference, however, is made to the work of Brodie, who was the first to demonstrate the connection.

W. D. H.

Thiocyanates in Nasal and Conjunctival Secretion. By O. MUCK (*Chem. Centr.*, 1900, ii, 1157—1158; from *Münch. med. Woch.*, 47, 1168—1169).—The presence of potassium thiocyanate can be shown in the nasal secretion as well as in the saliva. This, however, originates from the secretion of the conjunctiva. In ozæna, the amount here, and in the saliva, sinks.

W. D. H.

Solubility of Pigments in Fats and Soaps. By JOSEPH NERKING (*Pflüger's Archiv*, 1900, 82, 538—540).—The general conclusion arrived at is that the pigments recently used in experiments in fat absorption which are soluble in fats, are also soluble in neutral solutions of soaps.

W. D. H.

Anti-coagulating Agents. By ERNST P. PICK and KARL SPIRO (*Zeit. physiol. Chem.*, 1900, 31, 235—281).—A review of past work shows how numerous and diverse are the various organic substances and extracts that, like 'peptone,' produce a non-coagulable condition of the blood. Experiments with fibrin show that the products of peptic digestion, or of digestion with acid alone, have this power, but

that the products obtained by tryptic digestion, by digestion with alkali alone, or by autolysis, have no such power. From pure proteids, however (edestin, casein), no anti-coagulating agent is obtained by any method. The products formed from fibrin by acid or gastric digestion lose this action when they are purified. Thus pure proto-albumose and heteroalbumose are inert, but a mixture of the two does not lose its power when they are purified by the ammonium sulphate method, but it does so after treatment with alcohol. Treatment of the fibrin beforehand with alcohol does not hinder it from yielding the anti-coagulating agent on subsequent treatment with acid or gastric juice. This agent is, however, destroyed by alcohol in a weakly alkaline but not in an acid solution. Acid-albumin prepared from fibrin is inactive. Not only does 'peptone' lose its anti-coagulating power by such treatment, but its other actions (on blood-alkalinity, on lymph formation, on blood pressure, and in the production of narcosis) disappear also. The anti-coagulating substance, whatever it is, must be present in small quantity, and be very active. It is not characteristic of digestion products, but is contained in extracts of various tissues, particularly of the digestive organs, and these, especially if fresh, contain little or often no peptone. The name 'peptozyme' is suggested for this active substance, and the material in fibrin, liver, &c., from which it is derived, is termed 'peptozymogen.' Many authors distinguish the action of so-called peptone from such a substance as leech extract by saying that the latter contains an anti-thrombin, whilst the action of peptone is to first produce an anti-thrombin within the body by acting on some organ like the liver. This theory is discussed, and it is shown that the peptozyme has a direct anti-thrombic action on blood *in vitro*. It is also shown that peptozyme-immunity is independent of its anti-coagulating activity.

W. D. H.

Immediate Action of Intravenous Injection of Blood-serum. By THOMAS GREGOR BRODIE (*J. Physiol.*, 1900, 26, 48—71).—The intravenous injection of blood-serum from any source into a cat causes arrest of respiration, inhibition of the heart, and vascular dilatation. The effect is due to excitation of the pulmonary nerves, and the effect on the heart is reflex. It is abolished by section of the vagi, or of its pulmonary branches. Some degree of immunity is produced by repeated injections. The active substance is of proteid nature, of the albumin class, and is coagulated at 86°. It is produced only when the blood clots, but the interaction of the blood corpuscles is also necessary for its formation. Serum obtained from plasma is inactive.

W. D. H.

Injection of Tetanus Toxin and Antitoxin into the Sub-arachnoid Space. By FRANCIS RANSOM (*Zeit. physiol. Chem.*, 1900, 31, 282—304).—Injection of tetanus toxin or antitoxin into the sub-arachnoid space is quickly followed by the passage of these substances almost entirely into the blood-stream. An increase in the normal power of the central nervous system to neutralise the poison after sub-arachnoid injection of antitoxin does not occur *in vitro*. After injection of the toxin, the nerve substance is more poisonous, probably

because it contains more poison in its blood. After sub-arachnoid injection of the poison, a small part is found in the cerebro-spinal fluid, part in the blood and lymph, and part in the central nervous system. After intravenous or subcutaneous injection, little or none finds its way into the cerebro-spinal fluid. If the blood has high anti-toxic value, the cerebro-spinal fluid is also anti-toxic, but in a smaller degree. Much interest attaches to the fact that toxin and antitoxin pass from the blood to the lymph, but in the case of the cerebro-spinal fluid, the passage is in the contrary direction.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Biology of the Peptonising Bacteria of Milk. By OTTO KALISCHER (*Arch. Hygiene*, 1900, 37, 30—53).—The bacteria in milk, which are aërobic or facultative anaërobic, are not destroyed by heating at 90—95°, and form spores not easily destroyed by heat, are termed “peptonising” bacteria. In milk, they slowly form ammonia and cause a diminution of the lactose, decompose dextrose, but not fat, and convert casein into peptone. The enzyme produced by them is very similar to trypsin, except that in the fermentation of casein by it, aromatic hydroxy-acids are formed in addition to peptone, leucine, and tyrosine; it will invert cane sugar, but not lactose.

R. H. P.

Lactic Acid Fermentation and its Practical Use. By STANISLAUS EPSTEIN (*Arch. Hygiene*, 1900, 37, 329—359).—The ripening of cheese is due to the organisms which induce the lactic acid fermentation. Each kind of cheese is produced by the agency of special organisms, which act chemically by means of an enzyme, and cause the peculiar odour of the cheese. If pure cultures are to be employed in the preparation of cheese, it will therefore be necessary to choose these, not only with regard to the character of the bacteria inducing the acid fermentation in the butter, but also with regard to the peculiar kind of cheese required.

R. H. P.

Formation of Hydrogen Sulphide in Sewers, and the New Genus *Aërobacter*. By MARTINUS W. BEYERINCK (*Arch. Néerland Sci. Exact. Nat.*, 1900, [ii], 4, 1—18).—The author proposes to include in a new genus *Aërobacter* such bacteria as ferment sugar with the formation of hydrogen, carbon dioxide, and lævorotatory lactic acid. These are the agents which cause the formation of hydrogen sulphide from sulphur, sulphites, thiosulphates, and proteids. The formation of this gas, which is also a characteristic of the genus, is easily demonstrated by the introduction of a little white lead into the culture media (gelatin or agar). The bacteria reduce nitrates to nitrites, but not to ammonia; the addition of a small quantity of a nitrate to a culture medium containing sugar prevents fermentation, but does

not stop the development of the organisms, thus, in the preparation of Dutch cheese ("rijzers"), a small percentage (0.05) of saltpetre is added to hinder the formation of gas. The fermentation of indican, due entirely to organisms belonging to this genus (and induced by all the species composing it, with the exception of *A. coli* var. *commune* = *Bacterium coli* var. *commune*), results in the formation of dextrose and indoxyl, which in the presence of air is converted into indigo, the fermentation being due to the living organisms and not to an enzyme. The bacteria of this genus cannot transform sulphates into hydrogen sulphide, this reduction being brought about by *Spirillum desulfuricans*. The nauseous odours of putrefaction are not due to sulphides.

R. H. P.

Influence of Temperature on the Energy of the Decomposition of Proteid in Germination. By DMITRI N. PRIANISCHNIKOFF (*Ann. Agron.*, 1900, 26, 627—628; from *Ber. deut. bot. Ges.*, 1900, 18, 285. Compare Abstr., 1900, ii, 233).—The temperature most favourable to the growth of the embryo is 28°, whilst the energy of respiration continues to increase as the temperature is raised. The energy of the decomposition of proteid, and the formation of asparagine increases up to 35—37°; this decomposition does not depend on the growth of the embryo.

N. H. J. M.

Chemical Changes during the Evolution of Buds. By GUSTAVE ANDRÉ (*Compt. rend.*, 1900, 131, 1222—1225).—Buds of *Æsculus hippocastanum* were analysed at seven different periods from February 26, when they showed no development, to April 28. The total dry matter, nitrogen, amides, carbohydrates, cellulose, ash, potassium, calcium, phosphoric acid, and silica in 100 buds were determined at each date; also the percentage of water.

As in the germination of seeds, there was a considerable absorption of water. There was first a loss of dry matter, but by April 18 there was again a slight increase; subsequently there was a very rapid and great increase both in dry matter and total ash. The calcium remained almost the same up to April 18, whilst the potassium and phosphoric acid greatly increased; afterwards there was a great increase in all the ash constituents determined. The increase in the amount of potassium coincides with the appearance of the first leaves. The amounts of phosphoric acid and total nitrogen were both tripled at the time when the buds recovered their original weight (April 18). The amide nitrogen increased from the beginning; the soluble nitrogen is presumably transformed into insoluble proteid nitrogen. Up to April 18, the soluble carbohydrates showed a remarkable decrease (9.12 to 2.85); by April 23 and 28, the amounts were 6.01 and 17.92 respectively.

The above changes indicate that the evolution of buds may be compared with germination.

N. H. J. M.

Development of Etiolated Plants after Exposure to Light. By H. RICHME (*Compt. rend.*, 1900, 131, 1251—1253).—The plants were kept in darkness for different periods and afterwards exposed to

normal conditions. Similar plants were kept the whole time under normal conditions.

In the case of etiolated plants from small seeds, the growth of the stems was checked the moment the plants were exposed to light, the growth being then slower than that of normal plants; with plants from large seeds, the growth of the stems after exposure to light did not appreciably differ from that of normal plants. The length of stem of the full grown plant is abnormally great when the etiolation ceased before the exhaustion of the reserve substances of the seed, but abnormally short when the reserve substances have been almost all consumed at the time when the plants had access to light.

The leaf development of etiolated plants also becomes abnormally large after exposure to light when there is plenty of reserve substance.

The weight of the dry matter (stems and leaves) is less in plants which were etiolated and afterwards exposed to light than in normal plants. As soon as the plants are exposed to light there is a great loss of water as well as gain in dry matter. Etiolated plants which afterwards have access to light weigh less, but contain more dry matter than plants kept in darkness during the whole period.

The above results show the importance of seed reserves which, to a great extent, enable the plant to develop without chlorophyllic action.

N. H. J. M.

Hydrolysis and Utilisation of Raffinose by *Penicillium Glaucum*. By HENRI GILLOT (*Bull. Acad. Roy. Belg.*, 1900, 99—127).—In a solution containing a mineral acid, *Penicillium glaucum* secretes an enzyme capable of inverting raffinose; neutralisation does not prevent this secretion, but diminishes the rapidity of germination of the spores. The action of the enzyme is accompanied by an increased acidity of the solution, due to the production of oxalic and succinic acids. Using the enzyme either in the form of an aqueous infusion of the fungus, or of the precipitate obtained from this infusion by adding alcohol, the intensity of the inversion gradually diminishes, if care be taken to exclude foreign organisms. In a solution containing 2 per cent. of raffinose, but no other nutritive materials, inversion still occurs, but the germination of the spores is slow, and the morphology of the mould is modified.

In alkaline solution, germination is retarded, the action of soda being less than that of either potash or ammonia; subsequently, however, when the mould has developed, the secretion of enzyme is but little affected, the solution gradually becoming acid. W. A. D.

Chemical Processes in the Juice of *Arum Maculatum*. By MARTIN HAHN (*Ber.*, 1901, 33 3555—3560).—In the hope of throwing more light on the question of the cause of the heat developed by certain plants, the bulbs of *Arum maculatum* were divided so as to separate the upper or sterile from the lower or flower-producing parts, and these were then subjected to the process applied by Buchner to yeast-cells in isolating the cell-free juice.

The greenish liquids thus obtained, which were free from organised forms, were neutral at first, but finally developed a reddish tinge, and became acid in reaction. Both liquids decolorised a considerable

quantity of *N*/10 iodine solution, reduced Fehling's solution rapidly, and when heated deposited albumin. With alkalis, the liquids became bluish-green and with acids red.

In investigating the properties of the juices, 20 c.c. were brought into a flask fitted with a sulphuric acid valve, mixed with 0.5 c.c. of toluene, and the temperatures maintained at 25°; after the completion of the digestion the whole was rendered neutral, boiled, diluted to 100 c.c., filtered, and aliquot portions of the clear liquid were employed for the estimation of the contained nitrogen and sugars; the sterility of the liquids was assured.

It was found that the amount of dextrose in the liquids slowly increased at low temperatures, indicating that a diastatic ferment is present, a fact which was confirmed by observations of the sucrose inverting power of the residues obtained by evaporating the juice in a vacuum. The presence of a proteolytic ferment was inferred, as after several days digestion at 25°, the liquids no longer deposited albumin when boiled, and were free from dextrose.

The manner in which the dextrose is degraded has not been ascertained; small quantities of carbon dioxide appear to be evolved, but no alcohol could be detected.

Attempts have been made to prepare an active, pulverulent extract by evaporation of the liquids, but these have hitherto met with only partial success. A. L.

Toxicity of Sodium, Potassium, and Ammonium Compounds as regards Higher Plants. By HENRI COUPIN (*Ann. Agron.*, 1900, 26, 575—577; from *Rev. gén. bot.*, 12, 177. Compare *Ann. Agron.*, 26, 350, and Demoussy, *Abstr.*, 1900, ii, 161).—Young wheat plants were subjected to the action of 21 sodium salts, 22 potassium salts, and 13 ammonium salts. The results are given in a table showing the minimum amounts of the various salts per cent. which kill the plants.

Comparing the haloid salts, it is shown that the toxicity increases with the mol. weight of the halogen. As a rule, potassium salts are less toxic for plants than the corresponding sodium salts. Oxalates, especially potassium hydrogen oxalate, are very toxic; the toxic equivalent of potassium hydrogen oxalate is 0.0033, that of potassium oxalate 0.25 per cent.

With one or two exceptions, the toxicities of the analogous compounds of sodium, potassium, and ammonium are similar.

The toxic equivalents of the three chlorides (in the order as given) are: 1.8, 1.9, and 1.6; nitrates, 1.7, 3.0, and 3.9; carbonates, 1.1, 1.7, and 0.3; phosphates, 1.5, 6.0, and 0.4; sulphates, 0.8, 2.3, and 2.5. The toxicity of sodium hydrogen carbonate is 0.6. N. H. J. M.

Humic Acid and its Function in Nature. By HUGO BORN-TRAEGER (*Chem. Centr.*, 1900, ii, 1202; from *Oesterr. Chem. Zeit.*, 3, 516—517).—Humic acid in presence of water is capable of absorbing a considerable quantity of ammonia, which it retains with some obstinacy. The ammonia is removed, however, by the action of the acid of sprouting seeds, humic acid being regenerated. Under certain conditions, humic acid also attacks the plant fibres, forming

sugar and vegetable gum. By treating 100 grams of fibre with 20 of humic acid (Cassel brown) and 20 of water under pressure, 8 grams of sugar and 20 of gum were obtained, but the sugar was not formed even by prolonged boiling under the ordinary pressure.

E. W. W.

Cultivation of Barley. By AIMÉ PAGNOUL (*Ann. Agron.*, 1900, 26, 561—567).—Experiments were made in pots, to show the effect of nitrogenous manure and phosphate on the growth of barley in different soils, both with small and large amounts of water, to correspond with very dry and very wet seasons. The seeds were sown on March 5.

On May 7 a number of plants were removed from each pot. It was found that the development of the plants was greatest under the influence of much water, but that the percentage of dry matter was lower in these plants (9.6) than in those which had less water (12.6). Comparing the different soils, the clay soil gave the worst results. Nitric nitrogen was more abundant in the wet than in the drier soils; the sandy soil contained the most nitrate, and the clay soil much the least.

When the plants were cut at the end of July, the yields were found to vary in the same order as in the plants taken up in May. The yields of straw and grain, in the case of the plants which received much water, were about double those of the plants with little water. With nitrogenous manure, the yield of straw was above, the yield of grain below, the average; with superphosphate, the yield of straw was below, and the yield of grain above the average. Superphosphate gave much heavier grain than nitrogenous manure.

All the plants were attacked by rust, the effect of which was to greatly diminish the weight of the seed, whilst the percentage of nitrogen and phosphoric acid was very greatly increased.

N. H. J. M.

Influence of the [Mode of] Distribution of Manures on their Action. By J. M. POMORSKI (*Chem. Centr.*, 1900, ii, 1249; from *Zeit. landw. Versuchs. Wesens Oesterr.*, 3, 649—683). [Compare Berthault, *Abstr.*, 1900, ii, 753].—The results of field experiments with oats showed that the localisation of sodium nitrate in furrows increased the amount of nitrogen taken up, and that the utilisation of nitrate by oats depends on the distance of the manure from the plants.

In pot experiments, it was found that nitrate had the same effect, whether mixed with the first, second, or third 10 centimetres of soil, but that better results were obtained when the manure was mixed with the whole of the soil.

Further experiments were made, the results of which showed that the mode of distribution of manures affects assimilation and growth, and that oats and barley behave differently.

The subject is thought to be of practical importance, as manures may be economised by being applied in the manner best adapted for the various crops.

N. H. J. M.

Analytical Chemistry.

Perchloric Acid. By CARL HAEUSSERMANN and ALB. SIGEL (*Ber.*, 1901, **33**, 3598—3599).—The formation of a red coloration by the action of perchloric acid on aspidospermine and the strychnine alkaloids (Fraude, *Abstr.*, 1880, 69) does not take place when the acid is purified by conversion into the silver salt, or merely by the addition of a little hydrogen sulphide; the reaction is, however, produced when chlorine water or a persulphate is added to the purified acid.
T. M. L.

Estimation of Oxygen in Commercial Copper. By MAURICE LUCAS (*Bull. Soc. Chim.*, 1900, [iii], **23**, 900—904. Compare *Abstr.*, 1899, ii, 52).—Ten to twenty grams of the metal, contained in a porcelain boat, are covered with a sufficient amount of pure, finely divided tin to form an alloy containing about 20 per cent. of the latter metal, and heated at 900°, by means of an electric furnace, in a porcelain tube through which is passed a current of carbon monoxide free from oxygen and carbon dioxide. The carbon dioxide resulting from the combination of the oxygen contained in the copper with the carbon monoxide is collected and estimated just as in organic analysis. The addition of tin allows the operation to be carried out at a lower temperature than would be required if the copper were heated alone. In this process, arsenic and antimony are partly volatilised and condense in the colder part of the tube. A portion of the sulphur is converted into carbon oxysulphide, whilst nickel is volatilised as nickel carbonyl.
N. L.

Irregular Distribution of Sulphur in Pig Iron. By RANDOLPH BOLLING (*J. Amer. Chem. Soc.*, 1900, **22**, 798—799).—Attention is called to the irregular distribution of sulphur in pig iron. An instance is mentioned where the bottom of the mould contained 0.013 per cent. less sulphur than the top. To obtain a representative sample, it is necessary to drill a hole entirely through the sample pig and mix the drillings well before proceeding with the analysis.
L. DE K.

Estimation of Sulphuric Acid in the Presence of Iron. IV. By FRIEDRICH W. KÜSTER and A. THIEL (*Zeit. anorg. Chem.*, 1900, **25**, 319—322).—A polemical paper in answer to criticisms by T. W. Richards (*Abstr.*, 1900, ii, 472).
E. C. R.

Estimation of Nitrogen in Saltpetre. By O. BÖTTCHER (*Chem. Centr.*, 1900, ii, 1161; from *J. Landw.*, **48**, 287—289).—Von Wissell (*Abstr.*, 1900, ii, 685) obtained too low results by the method given by the author, who, however, has again obtained satisfactory results. Blank experiments will never differ to the extent of 0.25 c.c. of acid if pure chemicals and proper apparatus are used.

Zinc dust may be sufficiently freed from ammonia by treatment with water, but sodium hydroxide sometimes contains nitrates, or nitrites which are difficult to remove.
L. DE K.

[Estimation of Nitrogen in Saltpetre.] By L. VON WISSELL (*Chem. Centr.*, 1900, ii, 1161—1162; from *J. Landw.*, 48, 291—292).—A reply to Böttcher (preceding abstract). The author upholds his previous statement that Devarda's process is preferable to Böttcher's.

L. DE K.

The Bio-Chemical Arsenic Test. By G. MARPMANN (*Chem. Centr.*, 1900, ii, 1187; from *Pharm. Centr.-Halle*, 41, 666—672).—Ten grams of a mixture of equal parts of dry, powdered black and white bread are introduced into a 100 c.c. flask and thoroughly moistened with the suspected liquid. After closing the flask with cotton wool, the contents are sterilised by heating in steam; next day, the sterilisation is repeated, and when cold the mass is inoculated with *Penicillium brevicaulis* or an allied fungus. If arsenic is absent, an agreeable odour, resembling a beer-soup with bread, is noticed after some time, but, should there be arsenic, an odour of arsenic hydride is evolved; this may be diminished or even completely masked by the presence of certain compounds of phosphorus or sulphur, which yield evil smelling gases. An attempt to separate and identify the various gases was not satisfactory.

L. DE K.

Arsenic in Beer and Brewing Materials. By ALFRED C. CHAPMAN (*Analyst*, 1900, 26, 8—10), ALFRED H. ALLEN (*ibid.*, 10—13). REPORT OF THE COMMISSION TO THE MANCHESTER BREWERS' CENTRAL ASSOCIATION (*ibid.*, 13—15).—Beer has been found to contain arsenic owing to the use of arsenical brewing sugars. The arsenic contained in these materials was derived from arsenical sulphuric acid used in their manufacture. To detect the presence of arsenic in beer, the Manchester Committee gives the following instructions.

Two hundred c.c. of the beer are heated to boiling in a porcelain dish, 30 c.c. of pure, strong hydrochloric acid are added, and then a piece of pure, bright copper-foil, one-quarter by one-half inch in size, and the boiling is continued for 45 minutes. If, after that time, the copper remains bright, no arsenic is present. If a deposit has been formed, the foil is washed successively with water, alcohol, and ether, dried at 100°, and heated in a 2-inch reduction tube, the upper part of which should be warmed before the sublimation begins. If any sublimate is obtained, it must be examined under a magnifying power of 200 diameters. An arsenical sublimate shows well-defined octahedral or tetrahedral crystals.

Chapman and Allen operate in a similar manner, but the latter advises oxidising any sulphites that may be present by the addition of bromine water, a little cuprous chloride then being added to facilitate the reduction of the arsenic. If Marsh's test is employed, a little bromine water should be added to the beer to oxidise any sulphurous acid; the excess of bromine and the alcohol may then be removed by a few minutes boiling.

Brewing sugars are tested in a similar manner to beer.

L. DE K.

Estimation of Arsenic as Ammonium Magnesium Arsenate. By O. DUCRU (*Bull. Soc. Chim.*, 1900, [iii], 23, 904—910).—The author

has not obtained satisfactory results in the estimation of arsenic as the sulphide, and since all compounds of arsenic are readily converted into arsenic acid, whilst the transformation into arsenious acid is often difficult and incomplete, the estimation as ammonium magnesium arsenate is considered the most satisfactory of the methods in general use. The double arsenate should be dried to a constant weight by heating in the water-oven, this process taking at least 20 hours; irregular results are obtained if the salt is converted into magnesium pyroarsenate by ignition. The corrections usually given for the solubility of ammonium magnesium arsenate are too low. The results of a number of experiments are quoted to show that the arsenic contained in the washings is comparable in amount with that in the filtrate, and that the correction (1 milligram per 50 c.c.) must be applied to the combined liquids and not, as is usually the case, to the filtrate alone. N. L.

Composition and Analysis of London Purple. By JOHN K. HAYWOOD (*J. Amer. Chem. Soc.*, 1900, 22, 800—809).—London purple is not, as hitherto believed, mainly composed of calcium arsenite and an organic dye, but the greater part of the arsenic is present as calcium arsenate; free soluble arsenious oxide is also nearly always present, and very often also free lime.

The analysis presents some difficulties on account of the colouring matter and the presence of the arsenic in both states of oxidation. To estimate the arsenic, the following process is adopted. Two grams of the sample are dissolved in about 80 c.c. of water and 20 c.c. of hydrochloric acid at 60—70°, and the filtrate and washings made up to 300 c.c. One hundred c.c. of this are treated in a 500 c.c. flask with sodium hydrogen carbonate in excess, and then diluted with water and a few drops of ether (to prevent frothing) to the mark. Two hundred and fifty c.c. are filtered off, mixed with starch solution, and titrated with standard iodine; this gives the arsenious oxide in 50 c.c. of the original solution.

Another 50 c.c. of the original solution are heated to 80° on the water-bath, then taken off and mixed with 3 grams of potassium iodide. After the lapse of 15 minutes, the iodine liberated by the arsenic acid is titrated with *N*/10 sodium thiosulphate. To properly observe the end point, the author proceeds as follows.

The sodium thiosulphate is run in slowly, and occasionally a drop of the solution is added to a drop of starch paste. When, finally, this only gives the faintest blue, a little starch paste is added to the whole of the solution and the colour dissipated with a few drops of thiosulphate. The solution is immediately made alkaline with solid sodium carbonate, hydrochloric acid added to slight acid reaction, and the whole again rendered alkaline with sodium hydrogen carbonate. Starch paste is now added and *N*/10 iodine run in until the blue colour appears; the end point is easily noticed by placing the beaker on a white surface between the eye and the light and adding the iodine until a distinct purple colour appears. This titration gives the total arsenic calculated as trioxide; by subtracting the result of the previous titration, the arsenic existing as pentoxide is obtained.

Methods are given for the estimation of soluble lime and soluble arsenious oxide and arsenic acid (compare Abstr., 1900, ii, 758), and analyses are given of five commercial samples of the article.

L. DE K.

Analysis of Commercial Metallic Silicon. By B. NEUMANN (*Chem. Zeit.*, 1900, 24, 869—870, 888—889).—The principal impurities contained in commercial silicon are iron, aluminium, calcium, and an insoluble residue consisting of iron silicide, silica, and silicon carbide. In the better class samples made in the electric furnace the silicon amounts to 93—97 per cent., whilst inferior samples contain only from 70—80 per cent.

One gram of the extremely finely powdered sample is treated with 100 c.c. of a 10 per cent. solution of sodium hydroxide contained in a silver dish covered with a watch glass, and heated on the water-bath until no more hydrogen is evolved. The insoluble matter contains all the impurities mentioned except a little aluminium which has dissolved in the soda. On treating it with hot hydrochloric acid, a residue is obtained containing the iron silicide, silicon carbide, and silica; this is then heated in a platinum crucible and weighed, and if desired it may be further tested. The solution contains iron and aluminium, which are precipitated by ammonia and afterwards redissolved in hydrochloric acid; the filtrate contains the calcium, and occasionally magnesium, which are then estimated as usual. The main alkaline solution, which contains also the bulk of the aluminium, is saturated with carbon dioxide, or, better still, acidified with hydrochloric acid, and precipitated while hot with ammonia. The precipitate, consisting of alumina with some silica, is put into a porcelain dish, the hydrochloric acid solution of the mixed iron and aluminium hydroxides is added, the whole evaporated after addition of sulphuric acid and heated to render the silica insoluble, and then boiled with dilute hydrochloric acid. The filtrate is divided into two equal parts; in one half, the iron is estimated volumetrically, and in the other half, the joint iron and aluminium is precipitated with ammonia.

The silicon is obtained by difference.

L. DE K.

Method for the Rapid Estimation of Carbon in Steel. By ROBERT JOB and CHARLES T. DAVIES (*J. Amer. Chem. Soc.*, 1900, 22, 791—797).—This is a simplification of Sargent's apparatus (Abstr., 1900, ii, 574), in which all the advantages are said to be retained. The separate, water-jacketed copper oxide tube may be entirely eliminated by simply increasing the length of the combustion furnace to 9 inches, increasing the length of the combustion tube to 20 inches, and inserting closely rolled copper gauze, about 4 inches in length and thoroughly oxidised prior to use, into the combustion tube exactly as in the old method, placing pieces of clay pipe stems between the copper oxide and the end of the tube so as to prevent the former from being forced out of place.

It was found that, as regards the furnace, three bunsen burners each about $2\frac{1}{4}$ inches apart, having spreaders upon the tops, give sufficient heat to keep the porcelain tube at bright redness over

8 inches of its length, a thin sheet iron being placed just beneath the tube as a protection from the direct action of the flame. Under these circumstances, the condensing worm is no longer necessary. The moist sand tube has been replaced by a U-tube containing anhydrous cupric sulphate and cuprous chloride, as recommended by Blair, inserting beyond it a small bubble tube containing 10 c.c. of a saturated solution of silver sulphate in sulphuric acid of sp. gr. 1.4. As regards the oxygen used in the combustion, the authors have had no difficulty in procuring a commercial article which was free from carbonaceous impurities, but if the quality is doubtful, a separate appliance may be avoided by simply passing a copper tube through the combustion furnace, utilising the heat of the three burners. An apparatus of this nature is readily attached to the furnace by boring two quarter-inch holes in each side of the furnace just above and slightly to one side of the spreaders of the bunsen burners, running a seamless copper tube of $\frac{1}{4}$ inch outside diameter entirely through the furnace, out through the end, and then, parallel to the first, back to the opposite end, the tube being in such a position that the flame will not play directly upon it, but still will heat it to redness. The ends of the tube, after passing through the furnace, are bent down to the level of the desk, and then extended along to the connection of the oxygen supply beyond the three-way cock. In this way, the ends of the copper tube remain cool, and may be connected with the rubber tubes without there being any necessity for a water-cooling arrangement.

Other minor modifications are described.

L. DE K.

Chemical and Calorimetric Analysis of Fuel. By HERMANN LANGBEIN (*Zeit. angew. Chem.*, 1900, 1227—1238, 1259—1272).—A lengthy paper containing a very large number of full analyses of wood, peat, lignite (brown coal), briquettes, coals, anthracite and coke; also paraffin oil, petroleum, benzenes, &c.

It is stated that the heating values of these substances is better obtained by direct experiment than by calculation from the elementary composition. The author prefers using a Kröcker's bomb, the crucible of which is lined with platinum foil instead of being enamelled. Full particulars are given as to the best methods of operation and calculation.

L. DE K.

Detection of Metals by the Absorption Spectra of their Compounds with Alkanna. II. Rare Metals. By JULIUS FORMÁNEK (*Zeit. anal. Chem.*, 1900, 39, 673—693).—Besides the metals enumerated in a former communication (*Abstr.*, 1900, ii, 687), the following (in the form of chlorides or nitrates) alter the absorption spectrum of alkanna: cerium, lanthanum, neodymium, praseodymium, yttrium, erbium, thorium, zirconium, titanium, vanadium, indium, molybdenum, (solution of chloride in absolute alcohol), palladium, rhodium, and (?) ytterbium. The addition of a trace of ammonia produces a more intense absorption, generally accompanied by a change in the position of the bands, except in the cases of erbium, thorium, zirconium, titanium, vanadium, indium, and molybdenum, in which ammonia causes no change. An excess of ammonia usually causes

turbidity and again alters the spectrum. The spectrum generally consists of three bands, that nearest the red end being the strongest. The nitrates give spectra similar to, but not identical with, those of the chlorides. If a mere trace of the metallic salt is added, a spectrum is obtained with its bands in a different position and of different relative intensities. The spectra produced by the different metals are in no cases identical, but they are of little service for the detection of the metals when mixed, since their position is somewhat dependent on concentration, and the bands of one often overlap another.

Many interesting relations are noticeable between the wave-length of the principal absorption band and the position in the periodic system of the metal producing it.

M. J. S.

Analysis of Mixtures of Two Salts. By LUDWIG W. WINKLER (*Chem. Zeit.*, 1900, 24, 816).—To facilitate the analysis of two soluble salts by indirect analysis such as by titration with standard acid or standard silver solution, it is recommended to weigh such a quantity of the saline mixture that the excess of the volumetric reagent will at once show the percentage of the admixture.

The amount to be used in the test is represented by the equation $a = 100 : (1/e' - 1/e)$ in which e' represents the milligram equivalent weight of the admixture and e that of the chief constituent. For instance, to determine the amount of sodium carbonate in potassium carbonate, 2.279 grams of the mixture are titrated with *N* hydrochloric acid; every c.c. required in excess of 32.96 c.c. represents 10 per cent. of sodium carbonate.

L. DE K.

Determination of Unburnt and Overburnt Gypsum in the Plaster of Paris from the Kilns. By L. PÉRIN (*Compt. rend.*, 1900, 131, 950—952).—Plaster of paris as it comes from the kilns consists of natural gypsum which has escaped the action of the heat, gypsum which has become anhydrous on account of overheating, gypsum which has only lost part of its water and constitutes the active matter, and finally a proportion of other inert matter, silica, calcium and magnesium oxides, and ferric oxide and alumina. It is a well-known fact that the resistance of the plaster towards pulling, crushing, and bending is in inverse proportion to the inert matter which it contains. The following process is given by the author for the estimation of the unburnt and overburnt gypsum; the other constituents are determined by the ordinary methods.

The sample is powdered in an agate mortar, dried for two hours in an air-bath at 60°, and cooled in a desiccator. Five grams of the powder are then put into a tared porcelain or platinum dish and mixed with a slight excess of water to re-form gypsum; the mass is again dried at 60° to constant weight, and the quantity of water (A) which has combined with the active matter is thus found. Assuming that this active matter consists of $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, the total active matter (x) will be represented by 8.56 A .

Estimation of the Unburnt Gypsum.—The mass is now heated to redness and the loss in weight minus A represents the water (B) in combination with the unburnt gypsum. As this consists of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, its weight (y) will be represented by 4.8 B .

Estimation of the Overburnt Gypsum.—If a represents the sulphur trioxide corresponding with x , b the same corresponding with y and Q the total sulphur trioxide contained in the sample, then the trioxide corresponding with the overburnt gypsum (z) will be $Q - (a + b)$ and as 80 parts of sulphur trioxide correspond with 136 parts of calcium sulphate, z will be represented by $1.7\,q$.
L. DE K.

Methods for the Valuation of Materials for Improving Calcareous Soils and the Estimation of Readily Soluble Alkaline Earths and their Carbonates in Soils. By HEINRICH IMMENDORFF (*Zeit. angew. Chem.*, 1900, 1177—1184).—As the result of a large number of experiments, the author concludes that the calcium in calcareous soil improvers is best estimated volumetrically by means of standard acid and alkali; the results are satisfactory and the operation takes but little time. The same process also gives trustworthy results in the analyses of soils which are rich in calcium (or magnesium) carbonate. If the soils contain only a little calcium carbonate, the method becomes unsuitable when the object is not to estimate the readily soluble alkaline earths but only the carbonates, but the estimation of the alkalinity serves very well for the purpose of estimating readily soluble alkaline earths in the absence of carbonates.

As regards the estimation of calcium carbonate in soils by a carbon dioxide estimation, it is observed that the ordinary method may lead to grave errors when dealing with soils free from, or poor in, calcium carbonate. If a sample contains humus matters, heating during the estimation must be carefully avoided. The small quantity of carbon dioxide yielded by the humus does not affect the result when dealing with soils rich in carbonates. The author finally states that Stützer and Hartleb's ammonium chloride method (*Abstr.*, 1899, ii, 521) is untrustworthy when dealing with soils poor in calcium carbonate.

L. DE K.

Estimation of Lead in Cupriferous Minerals with Calcareous Gangue. By GEORGES GUEROULT (*Chem. Centr.*, 1900, ii, 1163; from *Ann. Chim. anal. appl.*, 5, 372—373).—The sample is dissolved in nitric acid and electrolysed according to Riche's directions. The copper which separates at the negative pole is weighed. The lead (as dioxide) at the positive pole is dissolved in nitric acid with addition of sugar, or in hydrochloric acid and then evaporated with sulphuric acid to obtain the lead as sulphate.

L. DE K.

Thiocyanates of Copper and Silver in Gravimetric Analysis. By R. G. VAN NAME (*Amer. J. Sci.*, 1900, [iv], 10, 451—457).—Copper thiocyanate has been supposed to retain 1.54 to 3 per cent. of water even after drying at 115° and, therefore, not to be well adapted for direct weighing. The author, however, finds that when collected on asbestos in a weighed crucible, it becomes perfectly anhydrous by drying for 2 or 3 hours at 110° . To ensure complete precipitation of the copper, the liquid should be precipitated with a fair excess of ammonium thiocyanate in the presence of ammonium hydrogen sulphite, and left for about 20 hours, unless there is practically no free acid, when a few hours suffice.

Silver cannot be precipitated as thiocyanate as the precipitate is soluble in excess of the reagent. On the other hand, thiocyanic acid may be conveniently precipitated with silver nitrate. After collecting the precipitate on an asbestos filter and drying at 115° , it becomes anhydrous and fit for direct weighing.

L. DE K.

Estimation of Mercury in Ammoniated Mercury and other Mercury Compounds. By C. T. BENNETT (*Pharm. J.*, 1900, [iv], 11, 575—576).—A solution of the mercury compound in water or dilute hydrochloric acid is treated with hypophosphorous acid (30 per cent.); reduction at once takes place with formation of a greyish-black precipitate of metallic mercury which, on warming, collects into a globule; the supernatant liquid is decanted on to a filter, which collects any small particles of mercury floating on the surface; the mercury is washed with warm water, dried at 100° , and weighed.

E. G.

Impregnation and Analysis of Antiseptic Dressing Materials. By F. URZ (*Chem. Centr.*, 1900, ii, 1181—1182; from *Pharm. Zeit.*, 45, 840—842).—The author (compare Abstr., 1900, ii, 762) reviews and criticises fourteen methods given for the estimation of corrosive sublimate in dressing materials. *Dressing materials containing iodoform.* After mentioning the processes of Greshoff, Lehmann, and Huss, the following method is recommended. The material is treated with alcoholic potash, the solution acidified with acetic or nitric acid, again neutralised with magnesium carbonate, and the iodine estimated either gravimetrically or volumetrically with silver nitrate. *Materials containing carbolic acid.* The phenol is converted into the tribromocompound, which is dried at 80° and weighed; or the phenol is estimated volumetrically according to Beckurts' process, or Vortmann's method. *Materials containing salicylic acid.* Five grams are extracted with pure ether free from acid and the ether residue is dried at 50 — 60° and weighed, or the material is extracted with alcohol and the solution titrated with $N/10$ potash and phenolphthalein. Equally accurate, although more complicated, is the iodometric process. One gram of the material is digested for half an hour in 100 c.c. of water, and 25 c.c. of the solution are treated in a glass-stoppered bottle with 100 c.c. of bromine solution (1.666 grams of potassium bromate and 5.939 grams of potassium bromide in 1000 c.c.) and 5 c.c. of strong sulphuric acid, and thoroughly shaken; after 15 minutes, 10 c.c. of a 10 per cent. solution of potassium iodide are added, and the liberated iodine titrated in the usual manner. *Materials containing boric acid.* Five grams of the cut up material are extracted in a 250 c.c. flask with 200 c.c. of a mixture of 1 part of glycerol and 19 parts of water, and the mixture is diluted to the mark with dilute glycerol of the same concentration. Fifty c.c. of the clear liquid are mixed with a sufficiency of glycerol, and titrated with $N/10$ potash, with phenolphthalein as indicator.

L. DE K.

Estimation of Manganese and Cobalt as Phosphates. By HENRY DRYSDALE DAKIN (*Zeit. anal. Chem.*, 1900, 39, 784—790).—The method employed by the author for the estimation of zinc as phos-

phate (Abstr., 1900, ii, 624) is equally serviceable for manganese and cobalt. The addition of ammonium chloride is not necessary, but it is desirable to nearly neutralise with ammonia any large excess of free acid that may be present, and to add at least 10 parts of ammonium phosphate for 1 part of the metal to be estimated. The amorphous phosphate, which is precipitated, changes into the crystalline, double ammonium phosphate during the 10—15 minutes heating; filtration may be commenced at any time after cooling for half an hour. The precipitate is washed with a hot 1 per cent. solution of ammonium phosphate, and then with dilute alcohol. After 2 hours drying at 100—105°, its weight becomes constant, and corresponds in each case with the formula $M''NH_4PO_4 \cdot H_2O$. Ignition with free access of air reduces the precipitate to pyrophosphate. Results of equal accuracy were obtained whether the precipitate was weighed in the one form or the other. M. J. S.

Estimation of Iron in "Ferrum Oxydatum Saccharatum" containing a large Percentage of Iron. By WILHELM GOHLICH (*Chem. Centr.*, 1900, ii, 1162—1163; from *Pharm. Zeit.*, 45, 815—816).—Two grams of the sample are mixed with an equal quantity of dry sodium carbonate, and the mixture ignited in a small platinum dish. The residual ferric oxide is then dissolved in hydrochloric acid, mixed with potassium iodide, and the liberated iodine titrated with standard sodium hydrogen sulphite.

The sample may, however, be tested with equally satisfactory results by the German official process for the estimation of iron in the 3 per cent. drug. L. DE K.

Estimation of Iron in Magnetite Ore by the Specific Gravity Test. By JOSEPH W. RICHARDS (*J. Amer. Chem. Soc.*, 1900, 22, 797—798).—Many magnetite ores are simply mixtures of magnetite and quartz. A table is given showing the percentage of ferrosferric oxide (or iron) and silica in magnetite with the corresponding specific gravity of the sample.

The specific gravity may be taken at the mine when a suitable pair of scales is at disposal; the inaccuracy caused by the use of a rough scale is compensated by the large quantity of ore (from 1 to 50 pounds) used in the experiment. The results are correct within a few per cent., and quite accurate enough for the purpose of grading.

L. DE K.

Iodometric Estimation of Chromic Acid. By KARL SEUBERT and A. HENKE (*Zeit. angew. Chem.*, 1900, 1147—1154).—After some introductory remarks by the first author, the article is devoted to "The action of potassium dichromate on potassium iodide in the presence of sulphuric acid." Tables and curves are given showing the influence of dilution, time of action, excess of acid, excess of either potassium iodide or dichromate, &c., on the amount of iodine liberated. The experiments were conducted by measuring the solution of the dichromate, then adding, first, the calculated volumes of water and solution of potassium iodide, and finally a definite amount of acid; this was then regarded as the starting point of the experiment. To obtain accurate results in the iodometric analysis of chromic acid, care

should be taken to add about 18 mols. of potassium iodide and 70—110 mols. of sulphuric acid (previously diluted) for 1 mol. of potassium dichromate. After a few minutes' action in a closed flask, the mixture is largely diluted with water to get rid of the green colour due to chromic sulphate, and the liberated iodine is then titrated with *N*/10 sodium thiosulphate, using starch as indicator. Any unavoidable excess of thiosulphate is in turn titrated with *N*/100 iodine.

L. DE K.

Estimation of Gold and Silver in Pyrites. By WILHELM BUDDËUS (*Chem. Zeit.*, 1900, 24, 922—923).—The usual process of scorifying with lead and cupelling the lead regulus does not give concordant results, and a not inconsiderable portion of the precious metals is retained by the slags. The following process is easier of execution and appears to give thoroughly trustworthy results.

One hundred to two hundred grams of the powdered sample are put into a Chamotte crucible of 70—140 c.c. capacity, the crucible is covered with a lid and heated for half or three-quarters of an hour in a muffle until a sulphur flame is no longer noticed. When cold, the contents are transferred to a beaker or casserole of 1—2 litres capacity and treated with 250—500 c.c. of hydrochloric acid (1:1) to dissolve the iron sulphide. The insoluble matter which, besides siliceous matter, contains all the gold and silver, is well washed, dried, and fused in a covered Hessian crucible with 50—100 grams of assay lead and 5—10 grams of dry borax; instead of the assay lead, 100—200 grams of a mixture of dry lead acetate and sodium carbonate may be used. The resulting lead regulus is then cupelled and the gold-silver button parted as usual.

L. DE K.

Estimation of Gold and Silver in Pyrites. By J. LOEVY (*Chem. Zeit.*, 1900, 24, 1114—1115).—The author criticises Buddëus' process (preceding abstract).

L. DE K.

Estimation of Calcium in Water. By GASSELIN (*J. Pharm.*, 1900, [vi], 12, 556—559).—Fifty c.c. of a *N*/100 solution of oxalic acid and two drops of a solution of ammonia are added to 50 c.c. of the water to be analysed. The mixture is then violently agitated, and after 10 minutes is filtered, and the amount of oxalic acid in the filtrate estimated by titration with *N*/100 potassium permanganate.

H. R. LE S.

Estimation of the Hardness of Water. By GIULIO MORGUO (*Chem. Centr.*, 1900, ii, 1186—1187; from *Giorn. Farm. Chim.*, 50, 440—445).—The author estimates the temporary hardness by titration with *N*/10 hydrochloric acid using methyl-orange as indicator; this neutralises any soluble carbonates. The permanent hardness is estimated by boiling the water with a known quantity of sodium carbonate, which causes the precipitation of the alkaline earths as carbonates; the excess of the alkali is then titrated in the filtrate.

L. DE K.

Action of Sodium *p*-Diazobenzenesulphonate on Iron Cystinate in Contaminated Water. By HENRI CAUSSE (*Compt. rend.*, 1900, 131, 1220—1222. Compare Abstr., 1900, ii, 457—458).—In

answer to Molinié's criticism of the author's test for cystine (this vol., ii, 42), further experiments were made which indicate that the presence of iron is essential to the formation of the orange coloration with sodium *p*-diazobenzenesulphonate. A contaminated water containing a considerable amount of cystine ceases to give the reaction after treatment with baryta water; the precipitate formed by this reagent retains all the iron cystinate, for on extraction with dilute potassium hydroxide solution a filtrate is obtained which, when rendered acid, develops the orange coloration. The cystinate is not decomposed by normal or basic lead acetate, for the precipitates produced by these reagents yield no cystine on extraction with dilute potash solution. Molinié's experiments on the production of the coloration with distilled water are not conclusive, for if the water placed in the distilling apparatus contained ferrous cystinate this substance would be found in the distillate, unless the distillation was performed in the presence of barium hydroxide. Phenol, catechol, and resorcinol, when treated with the diazosulphonate in the presence of traces of ferrous salts, also develop characteristic orange colorations.

The reaction is indicative of certain groupings rather than of a definite substance, for the orange coloration not destroyed by sulphurous acid is produced whenever water contains ferrous compounds containing the CSH or COS groups.

G. T. M.

Detection of Foreign Colouring Matter in Spirits. By CHARLES A. CRAMPTON and F. D. SIMONS (*J. Amer. Chem. Soc.*, 1900, 22, 810—813. Compare Abstr., 1899, ii, 530).—Fifty c.c. of the sample are evaporated on the water-bath nearly to dryness; the residue is washed into a 50 c.c. glass-stoppered flask, 25 c.c. of absolute alcohol are added, and when cold the liquid is diluted with water to the mark. After mixing, 25 c.c. of the solution are transferred to an ordinary globe-shaped separating funnel or flask with its stem above the stopcock expanded into a bulb the capacity of which up to a mark on the stem is 25 c.c.; the upper bulb should have a capacity of about 100 c.c. Fifty c.c. of ether are added, and the whole shaken at intervals for half an hour; when the layers have properly separated, the lower one is made up with water to the original 25 c.c. volume, which may be conveniently done by connecting the lower end of the apparatus with a rubber tube which carries water from an elevated flask, the inflow being regulated by the stopcock. The whole is again shaken, and the aqueous layer, after separation, is drawn off and compared in a tintometer with 25 c.c. of the liquid which has not been extracted with ether; from the difference in the two readings the percentage of colour soluble in ether is calculated. This consists chiefly of the colouring matter of oak wood. Genuine spirits yield 40—50 per cent. of their colour to ether, whilst spirits coloured by caramel or prune juice alone are not affected.

L. DE K.

Estimation of Dextrose and Dextrin in Commercial Glucose. By LÉON LINDET (*Bull. Soc. Chim.*, 1901, [iii], 25, 91—93).—The process described is based on (1), the estimation of the total carbon by combustion with cupric oxide in the usual manner; (2), the determination of the rotatory power. From the first of these two data, the

combined weight of the carbohydrates, calculated as $C_6H_{12}O_6$, is obtained, and from this, together with the rotatory power, the relative proportions of dextrose and dextrin are calculated. N. L.

Neumann's Modification of Fischer's Phenylhydrazine Test for the Detection of Sugar in Urine. By OTTO MARGULIES (*Chem. Centr.*, 1900, ii, 1188—1189; from *Berl. Klin. Woch.*, 37, 881—884).—The author has investigated this process (Abstr., 1900, ii, 248), and thinks it a very delicate one. Whilst the copper and bismuth tests no longer show sugar in urine when it falls to 0.05 per cent., the phenylhydrazine test distinctly shows the presence of 0.02 per cent. of sugar. Small quantities of albumin do not interfere, but large amounts of urates render the test less delicate. When the urine is very rich in phosphates, the test also becomes uncertain, unless the sugar is present to the extent of at least 0.5 per cent. L. DE K.

Estimation of Glycogen by the Pflüger-Nerking Method. By ERNST SALKOWSKI (*Pflüger's Archiv*, 1900, 82, 521—527). By EDUARD PFLÜGER (*ibid.*, 528—537).—Polemical articles chiefly directed to the question whether the former author has correctly described the method in his text-book. W. D. H.

Estimation of Tartaric Acid in Presence of Oxalic Acid. By M. PALLADINI (*Gazzetta*, 1900, 30, ii, 446—453).—On neutralising, by means of sodium hydroxide solution, a solution containing tartaric, oxalic, and citric acids in quantities proportional to their molecular weights, and adding calcium chloride, the precipitate obtained contains the oxalic acid and part of the tartaric acid as calcium salts, the solubility of the calcium tartrate being increased by the presence of sodium chloride. If acetic acid is added before the calcium chloride, the precipitated oxalate is found to contain a considerable proportion of tartrate, which cannot be removed even on heating the precipitate in a sealed tube with a large excess of glacial acetic acid. Silver nitrate precipitates oxalic acid but not tartaric acid from dilute solutions; if both acids are present, the precipitate consists of a mixture of the two salts. T. H. P.

Detection of "Saccharin" (*o*-Benzoic sulphinide) in Wine and Beer Free from Salicylic Acid. By F. WIRTHLE (*Chem. Zeit.*, 1900, 24, 1035).—To test for "saccharin" in wines which do not contain salicylic acid, 100—200 c.c. of the sample are evaporated to about 20 c.c. This is transferred to a separating funnel, the basin is rinsed with water containing a few drops of aqueous sodium hydroxide, and the whole strongly acidified with sulphuric acid. The liquid is shaken thrice in succession with 50 c.c. of ether, which is then filtered into an Erlenmeyer flask and after adding 10 c.c. of 0.5 per cent. aqueous sodium hydroxide and shaking, the ether is distilled off. The residue is evaporated in a small porcelain dish, 1 gram of solid sodium hydroxide is added, and the dish heated slowly in an air-bath to 215°; the heating is then continued for a quarter of an hour at 210—220°. The fused mass, when cold, is dissolved in warm water, acidified with sulphuric acid, and shaken with the usual mixture of

ether and light petroleum. The residue left on evaporation is dissolved in a few c.c. of water and tested with ferric chloride for salicylic acid, the presence of which is a proof of the presence of "saccharin." A very fine violet colour is obtained even if the 100 c.c. of the sample contain only 0.001 gram of saccharin. In the absence of this substance, there may be occasionally a dirty yellowish-red colour due to tannin compounds, but never a violet. When the process is applied to beers, a faint violet colour is occasionally obtained, even when the sample contains no "saccharin"; this is caused by the action of the alkali on the hop-tannins, traces of which pass into the ether; it may, however, be avoided by first adding to 100 c.c. of the sample a few c.c. of a saturated solution of copper acetate, followed by a solution of disodium hydrogen phosphate; the filtrate is then evaporated and treated as directed. Pure beer will then, at the worst, only cause a faint rose coloration.

L. DE K.

Apparatus for the Extraction of Liquids by Ether or Chloroform. By W. A. OSBORNE (*Proc. Physiol. Soc.*, 1900, ix—x).—Modifications of Soxhlet's apparatus are described and figured.

W. D. H.

Characters of Oil of Akee. By W. Garsed (*Pharm. J.*, 1900, [iv], 11, 691—692).—Oil of akee, obtained by expression from the arillus of the fruit of the akee tree (*Blighia sapida*), is a yellow, non-drying fat, partly liquid, and partly solid and granular; it melts at 25—35°, and begins to resolidify at about 20°. The following constants were determined, and compared with the corresponding characters of palm oil and olive oil. Sp. gr., 0.857 at 100°/15.5°; Hehner number, 93; saponification number, 194.6; Reichert number, 0.9; iodine number, 49.1; acid number, 20.1. The mixed fatty acids distil without decomposition at 220—225° under 13 mm. pressure, melt at 42—46°, and resolidify at 40—38°; their saponification number is 207.7, and their iodine number, 58.4. A partial separation of the acids was effected by means of their lead salts; the salt which is soluble in ether appears to yield oleic acid, whilst the insoluble salt furnishes a white, crystalline powder; the latter acid may be a mixture of palmitic and stearic acids, or, more probably, a homologue of these acids.

E. G.

Cedar-nut Oil. By LEO VON SCHMOELLING (*Chem. Zeit.*, 1900, 24, 815).—Specific gravity, 0.930; rise of temperature with sulphuric acid, 98°; Hehner number, 91.97; saponification number, 191.8; iodine number of the oil, 159.2, and that of the fatty acids, 161.3; acid number, 3.25, that of the fatty acids, 193; glycerol, 10.31 per cent.; volatile fatty acids, 3.77 per cent.; free fatty acids, 1.6 per cent.; total fatty acids, 95.74 per cent.; average molecular weight of the oil, 280, that of the acids, 290; acetyl number of the fatty acids, after 6 days treatment in a closed flask, 81.9; liquid fatty acids, 87 per cent.; unsaponifiable matter, 1.3 per cent.; solidifying point of fatty acids, 11.3°. From the high iodine figure of the liquid fatty acids (184), it follows that these consist mainly of linoleic acid, with but very little linolenic and oleic acids.

Kryloff, who examined the oil in 1898, found: Hehner number

93.33; saponification number, 191.8; iodine number, 149.5—150.5; acid number, 1.09; free fatty acids, 2.0 per cent. Kryloff's statement that, on keeping, a crystalline deposit of palmitic acid is obtained is confirmed by the author. The author proposes to investigate Kryloff's statement as to the oxidation products of the fatty acids.

In conclusion, it is stated that the oil cannot be used as a substitute for linseed oil.

L. DE K.

Estimation of Fat in Creams. By C. H. ECKLES (*Chem. Centr.*, 1900, ii, 1165—1166; from *Bull. Iowa Agricultural College Expt. Station Ames*, 52, 31—42).—The author states that the fat in creams may be estimated by the Babcock method, if they are first suitably diluted with water. When fresh, this may be done by measuring; but if the sample contains air-bubbles, or if it has become sour, it should be weighed. On account of the great viscosity, it is best to rinse the pipette with warm water. Owing to the diminished sp. gr., a correction must afterwards be made as follows. If the fat amounts to 10—12 per cent., 0.1 should be added; for 13—14, 0.2; for 15—17, 0.3; for 18—20, 0.4; for 21—23, 0.5; for 24, 0.6; for 25, 0.7; for 26—27, 0.8; for 28—29, 0.9; for 30, 1.0; for 31, 1.1; for 32—33, 1.2; for 35, 1.4; for 36, 1.5; for 37, 1.6; for 38, 1.7, and for 40, 1.8 per cent. extra fat. The percentages of fat obtained by weight and measure then practically agree.

L. DE K.

Agreement between Milk Solids actually determined and those found by Calculation. By GOTTWALT AMBUHL (*Chem. Zeit.*, 1900, 24, 871—872).—From the result of 116 experiments, it is again shown that there is a close relation between the milk solids obtained gravimetrically and those ascertained by calculation from the specific gravity and the fat. The presence of fat in very small or very large quantity does not affect this relationship.

In the author's experiments, the fat has been estimated by means of Gerber's acidobutyrometer, and for the calculation of the solids, Fleischmann's formula has been used.

Reinsch and Lührig (*Abstr.*, 1900, ii, 771) have stated that the result of the direct estimation of the solids is untrustworthy unless the milk is quite fresh; the author has tested several milks from one to two days old with equally satisfactory results.

L. DE K.

The Reichert-Meissl Number of Dutch Dairy Butter. By WILHELM KIRCHNER and R. RACINE (*Zeit. angew. Chem.*, 1900, 1238).—The authors having tested a large number of samples of undoubtedly genuine butter from dairies in Holland, state that, particularly in the spring and the autumn, the Reichert-Meissl number may be as low as 21.8—22.1. They observe that the samples were not prepared from the milk of only a few cows, but in their presence, from a very large quantity of mixed milk.

L. DE K.

Action of Sodium Ethoxide on Fats. By HENRIK BULL (*Chem. Zeit.*, 1900, 24, 814—815, 845—847. Compare *Abstr.*, 1900, ii, 250).—*Volumetric Estimation of Water in Alcohol.*—If a solution of sodium ethoxide in absolute alcohol is boiled with a fat free from acidity, no saponification takes place. If, however, water is present,

this decomposes the sodium ethoxide with formation of sodium hydroxide and a partial saponification takes place; from the amount of alkali consumed, the amount of water may be calculated. To make the experiment, normal sodium ethoxide is required, which is standardised by warming 10 c.c. with 5 c.c. of medicinal cod-liver oil in a reflux apparatus for half an hour; after boiling for 15 minutes, it is allowed to cool, mixed with 20 c.c. of ether, and titrated with $N/2$ hydrochloric acid, using phenolphthalein as indicator. When the experiment is now repeated with the addition of a known volume of a weaker alcohol, less acid will be required in the titration, and the difference multiplied by 0.009 represents the volume of water.

Estimation of Glycerol in Fats.—Three grams of the sample are heated on the water-bath in a 50 c.c. narrow, stoppered tube with 3 c.c. of $2N$ sodium ethoxide at 70° for 30 minutes. After cooling for half an hour in the air, 25 c.c. of ether are added, the whole is well shaken, and then diluted with ether to the mark. When the supernatant liquid is quite clear, 25 c.c. are pipetted off, diluted with 10 c.c. of alcohol and titrated with $N/2$ hydrochloric acid and phenolphthalein until the reddish colour has disappeared; no notice should be taken of any brownish colour. The remaining liquid in the tube is similarly titrated, but with this difference, that 5 c.c. of acid must be added all at once. The amount of glycerol is found by multiplying the difference in the titrations by 0.0092. The author admits that there is sometimes a great difficulty in noticing the end-reaction; perhaps a more suitable indicator may be found.

Preparation of dry alcohol.—The amount of water in a commercial sample of absolute alcohol is first estimated by the process described, a large quantity is then mixed with the necessary amount of metallic sodium and a little oil, and submitted to distillation. L. DE K.

Analysis of Bone-Fat. By H. MENNICKE (*Chem. Zeit.*, 1900, **24**, 917—918, 923—924).—*Estimation of water.*—Five grams of the well mixed sample are dried at 105° in a flat nickel or glass dish to constant weight; this is generally attained after 6 hours. It must be remembered that the fat always contains a little benzene, which has been used in its manufacture, so that the water found will be slightly in excess of the truth. *Foreign admixtures.*—These consist mostly of inorganic constituents, lime soaps, and dirt. The lime soaps are, however, more or less soluble in any of the usual fat solvents, so that the results of the fat estimation may be as much as 10 per cent. too high. The author, however, is of opinion that from a technical point of view the lime soaps are not really impurities, although the calcium oxide contained therein must be considered as such. From this it follows that for the technical extraction of the bones, carbon tetrachloride would be the best solvent, although benzene offers other advantages. *Ash.*—The previously dried sample is burnt in a weighed platinum crucible; the ash should not exceed 10 per cent., and it may be further tested if desired. *Estimation of fat.*—Carbon tetrachloride or chloroform is used as the solvent, and the weighed fat is then burnt and any ash allowed for. The results are sufficiently accurate for technical purposes. The process given by Shukoff and Schestakoff (*Abstr.*,

1899, ii, 191) may also be used. The estimation of fat in bones, particularly extracted bones, presents some difficulties, as the amount obtained depends on the nature of the solvent; benzene is perhaps the most suitable one. *Detection of foreign fats.*—Leather grease, horse fat, and neatsfoot oil are notoriously added. Their detection presents serious difficulties, but gross adulterations may be safeguarded against by the determination of the iodine number: Genuine bone-fat gives an average iodine number of 53; that of the substitutes is generally much higher.
L. DE K.

Testing of Bees Wax. By J. WERDER (*Chem. Zeit.*, 1900, 24, 967—968).—When 5 grams of the sample are used for the saponification test, it is necessary to boil for an hour and a quarter; this is best done in an Erlenmeyer flask placed on wire-gauze and heated over a rose-burner. Pure wax always yields a clear solution, which remains clear for a long time on adding excess of boiling water; paraffin and ceresin, if present, form a layer on the top. If the saponified wax is dried with sand and then extracted with ether in a Soxhlet apparatus, it yields from 48.55 to 53.08 per cent. of unsaponifiable matters. Samples which yield a very much larger extract may, therefore, be suspected to contain paraffin.
L. DE K.

Analysis of Wax. By KARL DIETERICH (*Chem. Zeit.*, 1900, 24, 995).—The author agrees with Werder (preceding abstract) that although 20 c.c. of *N/2* alcoholic potash are theoretically sufficient for the saponification of 5 grams of wax, it is absolutely necessary to extend the time of boiling to an hour and a quarter. If, however, 3 grams only of the sample are taken, the saponification is quite complete in half an hour.
L. DE K.

Rapid Method for the Detection of Aniline-orange in Milk. By HERMANN C. LYTHGOE (*J. Amer. Chem. Soc.*, 1900, 22, 813—814).—About 15 c.c. of milk are placed in a porcelain casserole and the same quantity of hydrochloric acid of sp. gr. 1.20 is added, while gently shaking the vessel to cause thorough mixing and break up the curd into coarse lumps. If the sample contains aniline-orange, the curd will be coloured pink, but if not, it will be white or yellowish.

The same solution may now be tested for formaldehyde, by adding a drop of ferric chloride and boiling. A solution containing 5 c.c. of a 10 per cent. solution of ferric chloride to 2 litres of hydrochloric acid may also be used when testing for aniline-orange; this renders further addition of ferric chloride unnecessary when afterwards testing for formaldehyde.
L. DE K.

New Form of Urinometer. By ANDRÉ JOB (*J. Pharm.*, 1900 [vi], 12, 417—420).—The decomposition of the urine by sodium hypobromite is effected in a closed flask of known capacity, and the increase of pressure produced by the evolved nitrogen is measured by means of a manometer which is fused to the neck of the flask. From this increase of pressure, the weight of evolved nitrogen, and, consequently, the percentage of urea in the urine, is readily calculated.

H. R. LE S.

Estimation of Urea. By AL. BRAUNSTEIN (*Zeit. physiol. Chem.*, 1900, 31, 381—388).—It is shown that in the presence of hippuric acid the Mörner-Sjoquist method of estimating urea is not applicable. Correct results are obtained if, after the evaporation of the ether and alcohol and addition of magnesia, crystalline phosphoric acid is added and heated with the mixture at 140—145° for 4½ hours. Hippuric acid is not decomposed by such treatment, and after the addition of potash the ammonia formed from the urea can be distilled off and estimated.
W. D. H.

Quantitative Estimation of Morphine by Reduction with Silver Nitrate. By C. REICHARD (*Chem. Zeit.*, 1900, 24, 1061—1062).—The author has found that a moderately concentrated solution of morphine sulphate, when warmed with an excess of silver nitrate, causes a precipitate of metallic silver in the proportion of 2 atoms of the metal for 1 mol. of the alkaloid. The silver is collected on a filter, washed, and finally ignited in a weighed porcelain crucible.

As most of the other alkaloids do not readily reduce silver nitrate, the method is suitable for estimating the amount of morphine in an alkaloidal mixture. If the morphine salt should contain acids which are precipitated by silver nitrate, such as hydrochloric, hydrobromic, or hydriodic acids, the precipitated silver should be washed with ammonia, or a solution of sodium thiosulphate.
L. DE K.

Assay of Nux Vomica. By F. C. J. BIRD (*Pharm. J.*, 1900, [iv], 11, 574—575. Compare Farr and Wright, *Abstr.*, 1900, ii, 778).—The alkaloids of *Nux vomica* seeds may be readily extracted by the maceration-pressure method with a solvent composed of amyl alcohol (1 vol.), chloroform (3 vols.), and ether (4 vols.); the strychnine and brucine are then separated as ferrocyanides by a modification of Farr and Wright's method. It is immaterial whether 5 or 10 c.c. of the liquid extract are assayed, or if the time allowed for the precipitation of the strychnine ferrocyanide is 2 or 6 hours.
E. G.

Methods of Estimating Proteid Nitrogen in Vegetable Matter. By G. S. FRAPS and J. A. BIZZELL (*J. Amer. Chem. Soc.*, 1900, 22, 709—717).—Stutzer's method of precipitating the proteids by means of copper hydroxide is open to fewer objections than other processes.

Bromine is not a suitable precipitant for proteids in vegetable materials (compare *Abstr.*, 1898, ii, 320). Extraction with hot water does not always give concordant results. Phosphotungstic acid at 60° precipitates about the same amount of nitrogen as copper hydroxide, but at 90° or 100° the precipitation is incomplete.
L. DE K.

General and Physical Chemistry:

Refractivity of the Inactive Gases. By WILLIAM RAMSAY (*Arch. néerland sci. exact. nat.*, 1900, [ii], 5, 356—359).—The refractivities were compared with air or hydrogen by means of the apparatus described by Lord Rayleigh (*Proc. Roy. Soc.*, 59, 203; Abstr., 1896, ii, 598). The results for the value of $\mu - 1$ compared with air are: helium, 0.1238; neon, 0.2345; argon, 0.968; krypton, 1.449; xenon, 2.364. By division by the density these values become respectively 0.0309, 0.0172, 0.0242, 0.0177, 0.0184; neon, krypton, and xenon yield almost the same number, which is considerably less than those for argon and helium. It is noticeable that the first and third element in other series (halogens or alkalis) give similarly a higher value than the other members. L. M. J.

Indices of Refraction of Solutions of Calcium Chloride. By GUSTAV J. W. BREMER (*Arch. néerland sci. exact. nat.*, 1900, [ii], 5, 202—213).—By means of a spectrometer, the indices of refraction were measured in the case of various solutions of calcium chloride for the hydrogen lines H_α , H_β , H_γ , and for the sodium line, the value for infinite wave-length being also calculated. The solutions varied in concentration from 19.6 to 7.0 per cent., but the results are not strictly comparable, as the temperatures varied from 13° to 20°. The refractive power was calculated by the Lorenz formula and found to differ but little from that of pure water; it appears to decrease slightly as the concentration increases. The indices of refraction are greater than that of water, and the difference, which increases slightly with the refrangibility of the light, is approximately proportional to the concentration of the solution. L. M. J.

Spectroscopic Notes concerning the Gases of the Atmosphere. By LORD RAYLEIGH (*Phil. Mag.*, 1901, [vi], 1, 100—105).—According to Gautier, hydrogen is present in the atmosphere to the extent of about 2 parts in 10,000. The author, by examining the spectrum of the spark between platinum electrodes in a chamber through which dry air or other gas could be passed, finds that the C line is present when the chamber is filled with dry air, but experiments with other gases render doubtful the assumption that this line is actually due to atmospheric hydrogen.

A simple form of apparatus is described in which, operating with 5—10 c.c. of air and employing only three Grove cells, the spectrum of argon may be readily obtained.

By passing a current of carbon dioxide through a porous porcelain tube and absorbing the issuing carbon dioxide, a gaseous residue is obtained consisting chiefly of the lighter constituents of the atmosphere in which the D_3 helium line is observed. The success of the experiment depends greatly on the precautions observed to avoid the presence of other gases which had not diffused into the stream of carbon dioxide.

L. M. J.

Infra-red Spectra of the Alkalis. By HANS LEHMANN (*Chem. Centr.*, i, 1901, i, 81; from *Arch. wiss. Phot.*, 2, 216—222).—Photographs of the ultra-red spectra of potassium, rubidium, caesium, calcium, barium, magnesium, and iron have been obtained by means of extremely sensitive silver bromide gelatin plates suitably dyed. The lines observed ranged from 760—900 $\mu\mu$ wave-length, and agree well with those calculated from Kayser and Runge's law. The original paper contains reproductions of several spectra and also of the infra-red band spectrum of the carbon arc as far as wave-length 820 $\mu\mu$.

E. W. W.

Weston Cadmium Cell. By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 380—382).—The author corrects the statement made in a previous paper (*Abstr.*, 1900, ii, 702), that the Weston cells used by Jaeger and Wachsmuth were metastable below 23°; it now appears that these cells are stable. This result, however, does not agree with certain dilatometer experiments, and the author reserves further criticism of the Weston cell until the behaviour of cadmium amalgams has been more thoroughly investigated.

J. C. P.

Electrode Potentials and Absolute Potentials. By N. T. M. WILSMORE and WILHELM OSTWALD (*Zeit. physikal. Chem.*, 1901, 36, 91—98. Compare this vol., ii, 2).—A discussion on the relative merits of the calomel and hydrogen electrodes as the starting point in the determination of potentials. Wilsmore holds (1), that the potential of the hydrogen electrode is more accurately defined than that of the calomel electrode; (2), that where acid or alkaline electrolytes are used, it is especially valuable. Ostwald points out that whilst in most cases knowledge of the relative potential is sufficient, there are cases where knowledge of the absolute potential is necessary (compare, for example, Ostwald, *Abstr.*, 1893, ii, 357); the potential of the calomel electrode is based on electrocapillary phenomena, and it is probable that the absolute value thus found is the correct one.

J. C. P.

Theory of the Decomposition Potentials of Fused Salts. By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1900, 25, 436—458).—It is not safe to apply the methods used for the determination of the decomposition potentials of substances in aqueous solution to fused salts, because assumptions which are correct in the case of solutions are not necessarily so in the case of fused salts, which differ from solutions (1) in their physico-chemical nature, (2) in the fact that metals dissolve in them, (3) in the much greater rapidity of diffusion and mixing by eddy-currents, (4) in the greater rate of depolarisation of the electrodes.

The author supposes that when a gradually increasing E.M.F. is applied to a fused salt (for example, lead chloride) through indifferent electrodes, metal is liberated at the cathode which is at first almost completely dissolved by the electrolyte, the polarisation at the cathode remaining very small. As the E.M.F. increases and with it the quantity of metal liberated in unit time, the solution becomes more concentrated and the rate of solution of metal smaller until finally

the rate of deposition of metal exceeds the rate of solution and the maximum cathodic polarisation is attained. The same process occurs at the anode, the halogen rapidly diffusing into the whole of the anodic electrolyte until this is saturated. If the liquids surrounding the electrodes are not separated, the dissolved metal and halogen rapidly reunite, hindering or preventing the attainment of the maximum polarisation. According to the arrangement of the apparatus, the maximum polarisation may be reached first at one or other of the electrodes or simultaneously at both of them, and therefore the curves representing the connection between reverse E.M.F. and the applied E.M.F. may have a variety of forms. The author gives several of the characteristic shapes of curve which, according to his views, are to be expected, and states that they agreed with curves obtained experimentally. They exhibit changes of direction which correspond to the changes of direction in the current-E.M.F. curves obtained by Garrard (this vol., ii, 54), and which he takes to indicate decomposition potentials. When the anode and cathode liquids are separated from each other, the curve shows no *per saltum* change of direction, but the current increases in proportion to the applied E.M.F., so that it would appear as though fused salts may be decomposed by any E.M.F. T. E.

Conductivities of some Double Salts as compared with the Conductivities of Mixtures of their Constituents. By CHARLES F. LINDSAY (*Amer. Chem. J.*, 1901, 25, 62—69. Compare Jones and Mackay, *Abstr.*, 1897, ii, 396; Jones and Ota, *Abstr.*, 1899, ii, 587; Jones and Knight, *Abstr.*, 1899, ii, 628).—The double salts studied were $\text{KCl}, \text{CdCl}_2$; $\text{K}_2\text{SO}_4, \text{NiSO}_4$; $(\text{NH}_4)_2\text{SO}_4, \text{MgSO}_4$. In each case, the conductivity of the double salt in concentrated solutions is slightly less than the conductivity of a mixture of the constituents having the same concentration as the double salt. J. C. P.

Modification of the Common Method of Determining Transport Numbers and Investigation of the Influence of Concentration on these Numbers for some Ternary Salts. By ARTHUR A. NOYES (*Zeit. physikal. Chem.*, 1901, 36, 63—83).—If the dissociation of potassium sulphate and barium nitrate proceeds in stages, and if the proportion of the intermediate complex ion (KSO_4' or $\cdot\text{BaNO}_3$) diminishes with dilution, this change should betray itself in a marked alteration of the transport numbers with dilution. In the electrolysis of such salt solutions, the hydrogen and hydroxyl ions produced at the anode and cathode respectively travel so rapidly that they soon reach the middle portion of the solution; the electrolysis can thus last only a short time, the total quantity of salt transported is small, and the accuracy of the results is unsatisfactory. The author has got over this difficulty by adding to the anode and cathode solutions, as the electrolysis proceeds, enough alkali and acid to prevent the formation of hydrogen and hydroxyl ions. The apparatus employed consisted practically of two U-tubes, whose adjoining limbs are bent horizontally and may be connected by indiarubber tubing. The salts investigated were potassium sulphate, barium nitrate, and barium chloride, each at

two concentrations, (1) 0.1 gram-mol., (2) 0.02 gram-mol. per litre. The following table gives the transport numbers for the cation at 25° :

| Concentration. | K ₂ SO ₄ . | Ba(NO ₃) ₂ . | BaCl ₂ . |
|----------------|----------------------------------|-------------------------------------|---------------------|
| 0.1 | 0.493 | 0.455 | 0.415 |
| 0.02 | 0.496 | 0.456 | 0.442 |

The error in these numbers is certainly not more than a unit in the third place. The numbers for potassium sulphate agree with, those for barium nitrate and chloride are widely different from, the values obtained by Hittorf. The author's values for barium chloride lie between those of Hopfgartner (Abstr., 1898, ii, 151) and those of Bein (Abstr., 1898, ii, 553).

From the alteration of the above numbers with the dilution, the author concludes that the concentration of the KSO₄' ions in a 0.1 mol. solution of potassium sulphate does not exceed 1 or 2 per cent. of the total concentration. In the case of barium nitrate, it seems that no intermediate complex ions are formed. The alteration in the transport numbers for barium chloride is considerable, but the direction of the variation is opposite to what would be observed if the intermediate BaCl ions dissociated on dilution. The author considers the case analogous to that of the halogen compounds of cadmium, and supposes that in a 0.1 mol. solution of barium chloride complex ions exist (for example, BaCl₃' or BaCl₄''), formed by the addition of chloride molecules to Cl' ions, and that these ions are dissociated more and more with increasing dilution.

On the basis of the above numbers, and with the help of Kohlrausch's data (compare Abstr., 1899, ii, 201), the ionic conductivities of Ba⁺⁺ and SO₄'' may be calculated; the most probable values are found to be 54.4 for Ba⁺⁺, and 68.3 for SO₄''.

J. C. P.

Calculation of Degree of Dissociation of strong Electrolytes.

By SVANTE ARRHENIUS (*Zeit. physikal. Chem.*, 1901, 36, 28—40).—The author discusses Jahn's work (Abstr., 1900, ii, 522, 707), and defends the old method of calculating the degree of dissociation from the conductivity. For a concentration cell of the type AgAgCl | dilute solution of KCl | concentrated solution of KCl | AgClAg, the relation holds; $V = 1.98 \times 10^{-4} T [\Sigma m i \log(c_1/c_0) + m(i_1 - i_0)/M]$ volt, where c_1, c_0 are the concentrations, i_1, i_0 van't Hoff's ionisation coefficients for the concentrated and dilute solutions respectively; m is the transport number of potassium and $M = \log_e 10$. When the values for the E.M.F. given by this equation are compared with Jahn's experimental results, the degree of dissociation being calculated from the conductivity, an excellent agreement is found. The method of calculating the degree of dissociation from the E.M.F. of concentration cells with the help of Nernst's formula is not trustworthy, since the unavoidable impurities are left out of account.

Exception is taken to Jahn's statement that van't Hoff's law is a direct consequence of Planck's equations; the author insists strongly on the prior importance of the formulæ and laws established by Raoult, van't Hoff, and others, and regards the formal thermodynamical treatment of the properties of solutions as purely secondary.

J. C. P.

Electromotive Force and Osmotic Pressure. By FRIEDRICH KRÜGER (*Zeit. physikal. Chem.*, 1901, 36, 87—90).—It is pointed out that the expression deduced by Leffeldt (this vol., ii, 4) for the E.M.F. of a concentration cell is really the same as that deduced by Nernst in 1892. Leffeldt's contention (*loc. cit.*) that the E.M.F. depends on the total osmotic pressure of the salt, and not on that of the metallic ions alone, is regarded as entirely wrong.

The paper contains also a reply to Leffeldt's criticism (see this vol., ii, 5). J. C. P.

Relation between Expansion and Melting Points of Metals. By LÉMERAY (*Compt. rend.*, 1900, 131, 1291—1293).—If the rectangular co-ordinates of a number of points are taken to represent linear coefficient of expansion and absolute melting point of a number of metals, it is found that these points lie near the hyperbola $\lambda T = \text{constant}$. As the cubical coefficient of expansion is approximately 3λ , it hence follows that the expansion between absolute zero and the melting point is equal for all these metals, or equal volumes of metals at absolute zero are also equal at the melting points. Lack of data prevents any rigorous test of the value of this generalisation. L. M. J.

Latent Heats of Vaporisation of some Carbon Compounds. By WLADIMIR F. LUGININ (*Compt. rend.*, 1901, 132, 88—89).—The following results were obtained :

| | Latent heat of vaporisation. | Specific heat. | |
|--------------------------|---------------------------------|-------------------|------------------------|
| Aniline | 104.17 | 0.5485 | between 176.5° and 20° |
| Methylethylacetoxime ... | 115.73 | 0.6503 | „ 151.5 „ 21.9 |
| Anisole | 80.30 | 0.4806 | „ 151.7 „ 20 |
| Butyronitrile | 115.25 | 0.5471 | „ 113.3 „ 21 |

The values obtained by Trouton's formula indicate that in the cases of aniline, anisole, and butyronitrile there is no polymerisation, whilst with methylethylacetoxime the presence of the hydroxyl group causes polymerisation of the liquid molecules as in the alcohols and acids, although in the former case the hydroxyl group is directly united with nitrogen, whilst in the latter it is united with carbon. C. H. B.

Vapour Pressures of Binary Mixtures in the Light of van der Waals' Theory. By PH. KOHNSTAMM (*Zeit. physikal. Chem.*, 1901, 36, 41—62).—A theoretical paper largely unsuitable for abstraction. The author considers that too little attention has been paid by workers on this subject to van der Waals' theory (*Zeit. physikal. Chem.*, 1890, 5, 133—173), especially to his proposition that for liquids miscible in all proportions the vapour pressure curves (that is, the vapour pressure as a function of the composition (1) of the vapour, (2) of the liquid) have only one maximum or one minimum. The vapour pressure curve for mixtures of benzene and carbon tetrachloride is in accordance with this rule, in spite of Linebarger's results (*Abstr.*, 1896, ii, 408). The treatment of the whole subject in the works of Ostwald, Nernst, and Bancroft is adversely criticised, and it is pointed out that the

formulae of Duhem, Margules (compare Zawidzki, this vol., ii, 6), Leffeldt, and others are simply applications of van der Waals' theory.

J. C. P.

Vapour Tension of Ternary Mixtures. By FRANS A. H. SCHREINEMAKERS (*Arch. néerland. sci. exact. nat.*, 1900, [ii], 5, 214—226).—If the composition of a mixture is expressed in the usual equilateral triangle, and if, for any value of pressure and temperature, the potential is represented by the height above a base plane, then surfaces are obtained representing the liquid and vapour; of which, owing to its lower potential, the liquid surface will be the lower. In the simplest case, all mixtures are homogeneous, and the liquid and vapour surfaces may cut in one line $a_2 b_2$; if a tangent plane be rolled along to touch both surfaces, the points of contact lie on the lines $a b$, $a_1 b_1$. Mixtures represented by points within the figure $a b a_1 b_1$ separate into liquid and gaseous phases, outside this figure only one phase exists. The effects of variation of pressure, the addition of one of the constituents, &c., are considered. Where heterogeneous liquid mixtures can exist, the form of the surfaces are somewhat different, and the following equilibrium fields are obtained: liquid phase, two liquid phases, liquid and gaseous phases, gaseous and two liquid phases, gaseous phase. Effects of variation of conditions are considered, but the diagrams are necessary for their elucidation.

L. M. J.

Mixtures of Hydrogen Chloride and Methyl Ether. By J. P. KUENEN (*Arch. néerland. sci. exact. nat.*, 1900, [ii], 5, 306—311).—Methyl ether and hydrogen chloride yield a mixture boiling at 2° , and hence form an example of a mixture with a maximum boiling point and a minimum vapour pressure. The author attempted to trace this minimum up to the critical temperature, but it was found that before this was reached chemical action proceeds rapidly with the formation of methyl chloride and water. Complete investigation was hence impossible, but the results indicate that the minimum pressure exists up to the critical conditions, and that addition of hydrogen chloride raises the critical temperature of methyl ether. The curves actually obtained are given and prolonged to form the probable complete curve. Above the boiling point the mixture of the vapours is accompanied by considerable contraction, but the question of the molecular condition remains doubtful, as the contraction may be explained by association or by a high attraction constant.

L. M. J.

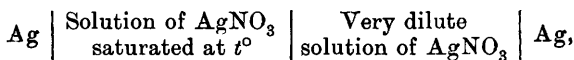
Heat of Formation of Mercaptans and Alkyl Sulphides. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 55—57).—The results obtained are summarised in the following table:

| | Heat of combustion (const. vol.). | Molecular heat of combustion (const. press.). | Heat of formation from elements. |
|---------------------------------------|--------------------------------------|---|--|
| Ethyl hydrosulphide (mercaptan) | 8313.6 cal. | + 517.2 Cal. | + 19.5 Cal. |
| Ethyl sulphide | 9191.5 „ | + 829.6 „ | + 33.7 „ |
| Amyl hydrosulphide | 9513.0 „ | + 992.0 „ | + 34.65 „ |
| Amyl sulphide | 10165.0 „ | + 1775.7 „ | + 67.5 „ |
| Allyl sulphide | 9348.3 „ | + 1068.1 „ | - 16.1 „ |

The thermal disturbance resulting from the substitution of oxygen for sulphur in the alkyl hydrosulphides and sulphides varies from +46.8 Cal. to +56.9 Cal. with a mean of +51.3 Cal., which approximates somewhat closely to the corresponding value in the case of water and hydrogen sulphide, carbon dioxide, and carbon disulphide, and metallic oxides and sulphides in solution. The differences between successive homologues is of the usual order of magnitude.

C. H. B.

Experimental Determination of the Limiting Heat of Solution. I. By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 327—332).—Two methods are given for calculating L the fictitious quantity of heat evolved when a gram-molecule of a salt dissolves in its own concentrated solution. (1) If a galvanic cell be constructed according to the scheme



the application of the equation $E_e = E_c/n\epsilon_0 + T.dE_c/dT$, leads to the relation $L = W - \epsilon_0/n_1.(E_c - T.dE_c/dT)$, where W is the first heat of solution and n_1 is the migration constant of the NO_3 ions. (2) For a cell of the type



The following relation holds: $L = W - 2\epsilon_0(E_c - T.dE_c/dT)$. The second method is preferable to the first, inasmuch as the values of migration constants in concentrated solutions are not known. The determinations of L made by the above methods will be published in a future paper.

J. C. P.

Heat of Solution of Resorcinol in Ethyl Alcohol. By CLARENCE L. SPEYERS and C. R. ROSELL (*Amer. J. Sci.*, 1900, [iv], 10, 449—450).—Resorcinol dissolves in large excess of ethyl alcohol with development of heat (see Speyers, *Abstr.*, 1896, ii, 410), and yet its solubility increases with rising temperature. This is shown to be consistent with the general law connecting the energy change of a reaction and the effect of rise of temperature; for heat is absorbed when resorcinol dissolves in a small quantity of alcohol, and dilution of a saturated solution is accompanied by rise of temperature. For a number of solutions of organic substances in water, ethyl alcohol, and other solvents, the authors have determined whether the final heat of solution is positive or negative; this was done by adding 5 to 10 per cent. of the pure solvent to the saturated solution.

J. C. P.

Liquefaction of Gaseous Mixtures. By F. CAUBET (*Compt. rend.*, 1900, 131, 1200—1202).—From the examination of the sets of complete isotherms for mixtures of carbon dioxide and sulphur dioxide (*Abstr.*, 1900, ii, 390), the following results are obtained. Every isotherm lower than the critical isotherm cuts the saturation curve in two points (1) a dew point, (2) a boiling point. The critical isotherm

cuts the saturation curve in a dew point and a critical point which may be regarded as either a dew point or a boiling point. Each isotherm of retrograde condensation cuts the saturation curve in two dew points, the first corresponding with the formation of liquid drops, the second with their disappearance. These results are in complete accord with the theoretical deductions of Duhem.

L. M. J.

Liquefaction of Gaseous Mixtures. Variation of the Concentration of the two Co-existent Liquid and Gaseous Phases along the Isothermals. By F. CAUBET (*Compt. rend.*, 1901, 132, 128—131).—If a mixture of carbon dioxide and sulphur dioxide be subjected to isothermal compression, then between two values, P_1 , P_2 , a two phase mixture is formed; the composition of each phase is determined solely by the values of the pressure and temperature. From the isothermals previously obtained (Abstr., 1900, ii, 390), these compositions can be deduced and curves are given showing the variation with pressure of the composition of both the liquid and gaseous phases, along isothermals from 59° to 89.6° .

L. M. J.

Viscosities of Mixtures of Liquids and Solutions. By CHARLES H. LEES (*Phil. Mag.*, 1901, [vi], 1, 128—147).—Assuming the liquid to move along the y axis and that the velocity varies along the x axis but not along the z axis, then assuming the liquid to be made up of separate layers between longitudinal planes, (1) perpendicular to the x axis, (2) perpendicular to the z axis, (3) of both the preceding sets, the following three formulæ for the viscosity of the mixtures are obtained: (1) $1/\eta = v_1/\eta_1 + v_2/\eta_2$; (2) $\eta = v_1\eta_1 + v_2\eta_2$; (3) $\log. \eta = v_1 \log. \eta_1 + v_2 \log. \eta_2$, where v_1 , v_2 are the volumes of the two constituents in 1 c.c. of the mixture. These three formulæ are tested by comparison with observed values for various mixtures obtained by Thorpe and Rodger, by Linebarger and by Wijkander. None of the formulæ is entirely satisfactory, the first giving the best results. The author finds, however, that an empirical formulæ, $(1/\eta)^m = v_1(1/\eta_1)^m + v_2(1/\eta_2)^m$ where m varies with different liquids, gives values in good accord with the observations both for liquid mixtures and for solutions. If also rise of temperature is regarded as due to the mixture with a hotter liquid, then the mixture formula can also become a temperature formula and the empirical formula given is found to reduce to Slotte's temperature formula $\eta = \eta_0/(1 + at)^{1/m}$.

L. M. J.

Osmosis of Liquids across Animal Membranes. By G. FLUSIN (*Compt. rend.*, 1900, 131, 1308—1309).—In the case of membranes of indiarubber, the velocity of osmosis of liquids has been shown to be dependent on the quantity of liquid absorbed in equal times (Abstr., 1899, ii, 204). The experiments are now extended to animal membranes, a portion of pig's bladder, well washed with ether and alcohol, being used. Determinations were made of the osmotic velocity, and of the quantity of liquid absorbed by the membrane in five minutes in the case of water, methyl alcohol, amyl alcohol, amyl acetate, chloroform, benzene, ethyl ether, and ethyl alcohol. This list is in descending order of magnitude for both constants, so

that the deduction [previously obtained for indiarubber membranes also holds good for animal membranes. L. M. J.

Hydrolysis of Salts. By CARL KULLGREN (*Bihang K. Svenska Vetensk.-Akad. Handl.*, 1900, 25, ii, No. 2, pp. 1—34).—The author has studied the hydrolysis of sucrose at different temperatures by means of aqueous solutions of various strengths of the following salts: cadmium chloride, cadmium nitrate, magnesium chloride, magnesium nitrate, zinc nitrate, lead nitrate, aluminium chloride, and aluminium nitrate. His results show that the relative increase of the dissociation constants of salts is more rapid at low than at high temperatures, whilst in the case of aluminium chloride solution (3/160 eqvts. per litre) such increase, which is considerable at lower temperatures, is no longer exhibited at 100°. This relative increase is also greater with weak solutions than with those more concentrated, a phenomenon which may be partly due to the greater inverting action of water on sucrose in the former case. The chlorides have in general about the same inverting power as the corresponding nitrates, although with cadmium chloride this power is about double that of the nitrate. The ratio between the inversion constants at 100° and at 85° has the value 3.78 for acids (acetic and succinic), but for salts it has higher values which in general vary but slightly with change of concentration; in most cases, this ratio has a high value when the inverting power is high. The amount of a salt hydrolysed increases with the dilution but follows no general rule; in the case of aluminium chloride solutions, the relation $x = k\sqrt{v}$ holds very approximately, x being the fraction of the total salt dissociated and v the dilution; for magnesium nitrate solutions, the amount of hydrolysis increases in arithmetical progression, whilst the dilution increases geometrically. The author's numbers are at variance with those of Long (*Abstr.*, 1896, ii, 414; 1897, ii, 547). T. H. P.

Researches on Solutions. By GREGOIRE WYROUBOFF (*Bull. Soc. Chim.*, 1900, 25, 105—130).—The act of dissolution is defined as the disaggregation or setting at liberty the molecules of a solid. This must be accompanied by the absorption of heat, and those cases of dissolution in which the reverse occurs are accompanied by secondary phenomena, such as polymorphous changes, combination with solvent, &c. The chemical molecule is not, however, the physical unit of the solid, as is rendered evident by cases of allotropy and polymorphism. These physical units the author terms 'crystalline particles,' and he considers that many mistakes have occurred by the assumption that by the act of dissolution they are decomposed into the chemical molecules. The present paper chiefly consists of arguments to prove that this assumption is unjustifiable, and that different crystalline particles of the same compound may exist in solutions. Solutions of natural anhydrous sodium sulphate or thenardite, and of the fused salt yield different crystals when precipitated by alcohol if freshly prepared, but if allowed to remain some time before precipitation this is not the case. Supersaturation is regarded as due to the existence of different hydrates or forms in the solution, and as necessary conditions for the

formation of supersaturated solution the author postulates (1) existence of at least two forms or states of hydration, (2) at higher temperatures, greater stability of the more soluble form.

Monopotassium orthophosphate yields supersaturated solutions, and is usually considered as monomorphic, but the author states that microscopic examination reveals the existence of two forms. Certain peculiarities of solubility are discussed, which are not in accord with the views generally entertained regarding solution. Cerium sulphate exists in six different states of hydration, and solubility observations have led to varying results. A saturated solution of anhydrous salt at 24° was obtained and found to deposit crystals of $3\text{CeSO}_4 \cdot 8\text{H}_2\text{O}$, the solution then containing 10 per cent. CeSO_4 . At 24° , however, the solubility of this compound is only 8.16 per cent. and precipitation by alcohol yielded also some crystals of $3\text{CeSO}_4 \cdot 9\text{H}_2\text{O}$. It was found also that if to the saturated solution of the octahydrate crystals of the nonahydrate are added, the concentration is increased and does not again decrease by addition of the octahydrate. It is even possible to obtain 12.3 per cent. solutions in equilibrium with the octahydrate crystals (solubility 8.16). Somewhat similar results were obtained with thorium sulphate, solutions of various concentrations being obtained in contact with the same crystals. A saturated solution of the crystals of potassium cadmium sulphate with $1\frac{1}{2}\text{H}_2\text{O}$ contains 42.5 per cent. anhydrous salt, but if crystals of the dihydrate are added they dissolve, and the concentration increases to 49.5 per cent. The author contends that these results indicate the actual existence in the liquid of the various kinds of crystalline particles, and further communications are promised. L. M. J.

Solid Solutions in Mixtures of Three Substances. II. By GIUSEPPE BRUNI and F. GORNI (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 326—332. Compare Abstr., 1900, ii, 197).—Freezing point determinations have been made of a large number of binary and ternary mixtures of the completely isomorphous compounds, *p*-dichloro-, *p*-chlorobromo-, and *p*-dibromo-benzene, and the curves for the ternary mixtures plotted on the ordinary triangular diagram. On the whole, the curves are regular, but near the angle representing the dichloro-compound they indicate a somewhat more complicated surface possessing points of minimum freezing point. T. H. P.

Reaction Velocity and Solubility. By WILDER D. BANCROFT (*Arch. néerland sci. exact. nat.*, 1900, [ii], 5, 46—48). The influence of solvents on reaction velocities is partly ascribable to viscosity. This is not the sole factor, however, and the author shows that solubility must also influence the velocity, and that decrease in the solubility of one of the reacting compounds tends to increase the rate at which the other is formed. Experimental evidence may, however, be difficult to obtain owing to the influence of other, as yet unknown, factors. L. M. J.

Inflammability of Thin Layers of Explosive Gases. III. By FRIEDRICH EMICH (*Monatsh.*, 1900, 21, 1061—1078. Compare Abstr., 1897, ii, 309, and 1899, ii, 12).—[With HEINRICH WALLAND.]—The temperatures of ignition of mixtures of electrolytic gas, with

varying proportions of nitrogen, hydrogen, or oxygen, have been determined by the Victor Meyer method. The addition of nitrogen scarcely alters the temperature at which electrolytic gas explodes; it is first slightly lowered and then slightly increased, the minimum being found with a mixture containing 30 per cent. of nitrogen. Somewhat similar results were obtained by the addition of hydrogen or oxygen.

[With V. VON CORDIER.]—Solutions of tricobalt tetroxide and of arsenic acid in concentrated hydrochloric acid have been shaken with hydrogen and air, but no differences were observed. The presence of ozone favours the ignition of electrolytic gas; for example, a mixture of 40 parts of hydrogen and 60 parts of 30 per cent. ozone is twice as inflammable as ordinary electrolytic gas.

The action of electric waves or Röntgen rays does not increase the inflammability of electrolytic gas. It is impossible to say whether the action of an excess of chlorine or oxygen in raising the inflammability of these gaseous mixtures is due to the small conductive coefficient of these gases or to the readiness with which the molecules of these gases are dissociated.

J. J. S.

Influence of Pressure in Phenomena of Chemical Equilibrium.

By OCTAVE BOUDOUARD (*Compt. rend.*, 1900, 131, 1204—1206).—The author has previously shown that the reaction $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$ proceeds as a reversible reaction in accordance with dynamical deductions (Abstr., 1900, ii, 199). The experiments were all conducted at atmospheric pressure, and are now supplemented by determinations at lower pressures which are completely in accord with the previous results, and again verify the formula then given.

L. M. J.

Equilibrium of Mixed Crystals with the Vapour Phase. By

H. W. BAKHUIS ROOZEBOOM (*Arch. néerland sci. exact. nat.*, 1900, [ii], 5, 360—365).—In a plane diagram for pressure against percentage composition, the equilibrium of mixture and vapour may be represented at any definite temperature, so that by the addition of a temperature axis surfaces are obtained representing the equilibrium at all temperatures. With diagrams representing these surfaces, the author considers the cases where between certain temperatures mixed crystals may be formed.

L. M. J.

Theory of Chemical Catalysis. By CONSTANTIN ZENGELIS (*Ber.*, 1901, 34, 198. Compare Euler, this vol., ii, 57).—A claim for priority.

T. M. L.

Platinum Catalysis: Observations on Gas Cells. By RUDOLF HÖBER (*Pflüger's Archiv*, 1900, 82, 631—640. Compare Bredig and von Bernick, Abstr., 1900, ii, 213).—The author finds that the substances which influence the catalytic action of colloidal platinum reduce the electromotive force of an oxygen-hydrogen element with platinum electrodes. The action only occurs at the oxygen electrode, and is probably due to the formation of complex platinum salts.

Reference is also made to the bearing of these facts on the action of poisons on organic ferments.

J. J. S.

Molecular and Ionic Reactions. By PAUL ROHLAND (*Chem. Zeit.*, 1900, 24, 1014—1016).—The author emphasises and illustrates the difference between molecular and ionic reactions, especially as regards their velocity (compare Abstr., 1900, ii, 468). J. C. P.

A Small Laboratory Furnace. By ALBERT BRUNO (*Compt. rend.*, 1901, 132, 276—277).—The crucible is suspended in the middle of two truncated cones formed of iron wire gauze lined with asbestos cardboard several millimetres thick, and placed base to base. The lower cone is about twice as long as the upper one, and its truncated apex is a short distance above the orifice of the Bunsen burner.

C. H. B.

Apparatus for the Extraction of Solutions by means of Liquids of a Lower Specific Gravity. By C. A. NEUFELD (*Zeit. Nahr.-Genussm.*, 1901, 4, 15—16).—This is a modification of Bremer's apparatus. It essentially consists of an inner glass cylinder and an outer glass jacket. The first, which holds about 300 c.c., is intended for the solution to be extracted. After the solution has been put into the cylinder, a thistle funnel is introduced the stem of which ends in a ring with small openings. The solvent, which condenses in a Soxhlet condenser, drops into the funnel and there gradually displaces the solution to be extracted, until it finally passes in minute drops through the ring-holes, when it charges itself with the soluble matter. It then collects on the surface and runs through a tube into the distilling flask. An extraction is generally completed within 2 hours and a half.

L. DE K.

Inorganic Chemistry.

Action of Iodine and Bromine on Chlorine Heptoxide and Perchloric Acid. By ARTHUR MICHAEL and WALLACE T. CONN (*Amer. Chem. J.*, 1901, 25, 89—96. Compare Abstr., 1900, ii, 471).—It is stated that no reaction is known which offers the slightest evidence that bromine or iodine is capable of directly replacing chlorine in its oxy-acids (compare Potilizin, Abstr., 1888, 220).

In the preparation of chlorine heptoxide, it is advisable to cool the retort containing the phosphoric oxide to temperatures below -10° , and to keep it at that temperature for several hours; the mixture may be then very slowly warmed until about two-thirds of the heptoxide has passed over, the receiver is then changed, and the temperature gradually raised to 85° . By this process, the danger of an explosion is greatly reduced. The product of the action of iodine on chlorine heptoxide is a white solid, which, when heated under reduced pressure at 100° gives off an oily liquid and leaves a residue of iodine pentoxide. The oily liquid dissolves in water, giving perchloric acid. The reaction between iodine and chlorine heptoxide is apt to be violent, and explosions can easily result.

Iodine and perchloric acid do not react so vigorously, and the product is a yellow, crystalline substance, HI_7O_3 , which is very hygroscopic.

Kaemmerer's results (*Ann. Phys. Chem.*, 1869, 138, 406) cannot be confirmed; the only product obtained by the action of iodine on aqueous solution of perchloric acid is iodic acid. J. J. S.

Phosphorus Suboxide. By AUGUST MICHAELIS and K. VON AREND (*Annalen*, 1901, 314, 259—275. Compare Abstr., 1900, ii, 137).—It has been frequently observed that analyses of phosphorus suboxide give too high a percentage of phosphorus. During an investigation devoted to the elucidation of this point, the authors have again examined phosphorus suboxide derived from phosphorus and from hypophosphorus acid, because Chapman and Lidbury (*Trans.*, 1899, 75, 973) expressed the view that the substance precipitated by dilute acids from a solution of phosphorus in alcoholic potash was merely amorphous phosphorus, one reason for this conclusion being the fact that red phosphorus, when prepared by exposing white phosphorus to light, dissolves quite readily in alcoholic potash diluted with water.

The authors, however, have been unable to prepare by this method a specimen of red phosphorus giving nearly theoretical results on analysis. They find that a dry solution of white phosphorus in carbon disulphide yields a specimen containing sulphur and carbon, a trace of water giving rise to a product which contains oxygen; red phosphorus obtained from a solution in carbon tetrachloride contains carbon. When white phosphorus is placed under water and exposed to the action of light, almost pure phosphorus suboxide is produced.

The paper contains full details of the experimental methods employed in the investigation. M. O. F.

Combination of Boron Bromide with Phosphorus Chlorides. By TARIBLE (*Compt. rend.*, 1901, 132, 83—85).—Boron bromide combines with phosphorus trichloride at the ordinary temperature, yielding a colourless, crystallisable compound, $\text{PCl}_3\cdot 2\text{BBr}_3$, which melts at about 58° , but sublimes at 40° , and decomposes before it boils.

In sealed tubes at about 150° , phosphorus pentachloride yields an analogous compound, $\text{PCl}_5\cdot 2\text{BBr}_3$, which forms colourless crystals, sublimes at 100° , and melts and begins to decompose at about 151° .

Both compounds dissolve in boron bromide (from which they can be crystallised) and in carbon disulphide, but not in light petroleum or vaselin oil. They are readily decomposed by water, absorb ammonia with considerable development of heat, and are attacked by oxygen at a red heat.

No other compounds of the same proximate constituents are formed under similar conditions, and the compounds formed by the phosphorus chlorides are not analogous to those formed by the bromides.

C. H. B.

Action of Boron Bromide on the Phosphorus Iodides and the Haloids of Arsenic and Antimony. By TARIBLE (*Compt. rend.*, 1901, 132, 204—207).—The double bromiodide, $\text{P}_2\text{I}_4\cdot 2\text{BBr}_3$, is obtained in the form of golden-yellow crystals by adding boron

bromide to a carbon disulphide solution of the di- or tri-iodide of phosphorus; in the latter case, the reaction being attended by the liberation of iodine; the compound evolves iodine at 130° and melts at 145° ; it dissolves in boron bromide, carbon disulphide, and chloroform, but not in light or heavy petroleum. The substance, on heating, burns in oxygen, yielding bromine, iodine, and the anhydrides of phosphorus and boron; it is decomposed by chlorine or sulphur vapour, but may be distilled without alteration in a current of hydrogen. The bromoiodide is decomposed by water with the production of phosphorous, boric, hydriodic, and hydrobromic acids; it absorbs ammonia gas, yielding a white, amorphous substance. When boron bromide is mixed with the trichloride of arsenic or antimony, a double decomposition takes place, resulting in the formation of boron chloride and the corresponding bromide of arsenic or antimony; antimony pentachloride under these conditions yields the tribromide and bromine. There is no interaction between boron bromide and the triiodides and tribromides of arsenic and antimony. G. T. M.

[Sulphides in] Bone Black. By F. STOLLE (*Zeit. Ver. deut. Zuckerind.*, 1901, 22—33).—Bone black does not, as is generally believed, contain calcium sulphide, and when heated, the calcium sulphate present is not reduced to sulphide, but gives up part of its sulphur, which forms ferrous sulphide with the iron reduced from the ferric oxide always present; if the amount of calcium sulphate present in bone black be increased, formation of calcium sulphide may occur. The diminution of the carbon content of bone black used in sugar refining is ascribed mainly to interchange taking place among the carbon-forming substances, and to a combustion of organic material.

T. H. P.

Action of Hypochlorous Acid on Metallic Chlorides. By W. VON TIESENHOLT (*J. pr. Chem.*, 1901, [ii], 63, 30—40; and *J. Russ. Phys. Chem. Soc.*, 1900, 32, 756—766).—When a solution of sodium chloride is treated with a small quantity of hypochlorous acid and evaporated to dryness, under certain conditions a residue is obtained which gives an alkaline reaction with phenolphthalein; the same result is observed with potassium chloride or barium chloride. If a stream of carbon dioxide is led into a strong boiling solution of barium chloride, and a solution of hypochlorous acid added drop by drop, barium carbonate separates after a certain time and at a definite concentration of the solution. If anhydrous calcium chloride is dissolved in the smallest possible quantity of hypochlorous acid solution, an energetic evolution of chlorine at once takes place; if carbon dioxide is now led into the boiling solution, a precipitate of calcium carbonate is immediately produced; when the solution is heated for a longer time without the introduction of carbon dioxide, calcium hydroxide separates, and the solution becomes strongly alkaline.

The conditions under which metallic hydroxides are produced from hypochlorous acid and chlorides are those which, according to Foerster and Jorre (*Abstr.*, 1899, ii, 278), favour most the formation of chlorates. The author considers that the production of chlorates under these conditions is preceded by the formation of alkali hydroxide, which is con-

verted by chlorine, first into hypochlorite and finally into the chlorate. The action of hypochlorous acid on metallic chlorides may be expressed by the equation, $\text{HClO} + \text{NaCl} = \text{NaOH} + \text{Cl}_2$, and the reaction between metallic hydroxides and chlorine may be regarded as reversible according to the equation, $2\text{NaOH} + \text{Cl}_2 \rightleftharpoons \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O}$. The paper concludes with a discussion of the bearing of these facts on the formation and constitution of bleaching powder. E. G.

Preparation and Properties of Hydrates of Sodium Peroxide. By GEORGE F. JAUBERT (*Compt. rend.*, 1901, 132, 86—88).—When sodium peroxide is placed in a moist atmosphere free from carbon dioxide, it absorbs somewhat more than three times its weight of water without decomposing and without becoming pasty, and in this way the hydrates $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$, as well as intermediate hydrates hitherto unknown, can readily be obtained. The hydrate, $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$, was prepared in large quantity and forms a white, snow-like mass, readily soluble in water at the ordinary temperature, without any decomposition and with considerable reduction of temperature. It is less soluble in water at 0° , and this fact can be utilised to obtain it in a crystallised form. It dissolves in somewhat concentrated acids without notable elevation of temperature and yields solutions of hydrogen peroxide of remarkable stability. This hydrate is very stable at the ordinary temperature, but begins to decompose at $30\text{--}40^\circ$ and is completely decomposed at $80\text{--}100^\circ$ (compare this vol., ii, 96). C. H. B.

Sodium Peroxide. By ROBERT DE FORCRAND (*Compt. rend.*, 1901, 132, 131—133).—The results obtained by Jaubert (this vol., ii, 96) have been already published by the author (compare *Abstr.*, 1899, ii, 95). G. T. M.

Ammonium Amalgam. By ALFRED COEHN (*Zeit. anorg. Chem.*, 1900, 25, 430—435).—The fact that the gas evolved by ammonium amalgam consists of ammonia and hydrogen in the ratio $\text{NH}_3 : \text{H}$, points to the existence of ammonium in it. At the ordinary temperature, however, the amalgam does not precipitate metals such as copper and silver from solutions of their salts. When solutions containing salts of the alkali metals are electrolysed with an oxygen anode and a mercury cathode, a change of direction of the current—E.M.F. curve occurs at 1.52 volts, due to the discharge of hydrogen ions; a second change of direction is also found at a lower potential, which depends on the nature of the alkali metal. For ammonium this second point is found at 1.24 volts in complete analogy with the alkali metals.

Ammonium amalgam, prepared and preserved at 0° , does not swell up in the usual way; the evolution of gas only takes place when it is warmed. When such an amalgam is placed in a solution of copper sulphate at 0° in electrical connection with a plate of platinum, copper is deposited on the platinum and copper amalgam is formed. The objection that the reduction might be due to hydrogen is met by the fact that cadmium and zinc, metals which are not precipitated by hydrogen, may also be precipitated from their solutions by cold

ammonium amalgam. The metallic nature of ammonium is, therefore, beyond doubt. T. E.

Allotropic Modifications of Silver. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 234—241).—The author has measured the heat developed when different forms of silver are dissolved in a large excess of mercury, the results being calculated to 108 grams of silver :

| | |
|--|-------------|
| Hammered silver in thin sheets..... | + 2.03 Cal. |
| The preceding variety heated in oxygen at 550° | + 0.47 „ |
| Electrolytic silver in brilliant, acicular crystals | + 0.10 „ |
| Silver precipitated from the nitrate by copper and dried at the ordinary temperature over sulphuric acid in a vacuum | + 1.19 „ |
| Silver precipitated in the same way, but dried at 120° | + 0.76 „ |
| Silver precipitated in the same way, dried at 120°, and heated to dull redness..... | + 0.08 „ |

It is evident that the various forms of the metal show considerable differences, which will give rise to different heats of formation of compounds prepared from them. For example, the maximum difference of 2 Cal. corresponds with a difference of 4 Cal. in the heat of formation of silver oxide, and 8 Cal. in the heat of formation of the suboxide, and in only one of the above cases would the heat of formation of the oxide be identical with the generally accepted value (7 Cal.). In the case of copper, as well as silver, and especially in the case of iron, the molecular condition of the metal is a factor of great importance in determining the thermal disturbance that will accompany a particular combination or interaction. C. H. B.

Compounds of Silver and Mercury. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 241—243).—Silver amalgams, prepared by direct combination of the metals, or by the action of mercury on solutions of silver nitrate, were dissolved in excess of mercury, and the thermal disturbance was measured. The results were: $\text{HgAg} + 0.33 \text{ Cal.}$, $\text{Hg}_2\text{Ag} - 0.50 \text{ Cal.}$, and $\text{Hg}_7\text{Ag}_6 - 0.58 \times 6 \text{ Cal.}$. In the first case, there is an initial absorption of heat which, however, is more than neutralised by the subsequent development of heat. The heats of formation of the amalgams calculated from these results are :

| | Ordinary silver in thin sheets. | Crystallised silver. |
|--|------------------------------------|----------------------|
| $\text{Hg} + \text{Ag} = \text{HgAg}$ | + 2.36 Cal. | + 0.23 Cal. |
| $\text{Hg}_2 + \text{Ag} = \text{Hg}_2\text{Ag}$ | + 1.53 „ | - 0.40 „ |
| $\text{Hg}_7 + \text{Ag}_6 = \text{Hg}_7\text{Ag}_6$ | + 2.17 $\times 6$ „ | + 0.24 $\times 6$ „ |

If the mercury is taken as being solid, these values must be reduced by 0.55 Cal. for each atom of mercury. C. H. B.

Action of Silver Salts on Ammonium Persulphate Solution. By HUGH MARSHALL (*Proc. Roy. Soc. Edinburgh*, 1900, 23, 163—168).—Solutions of potassium persulphate and silver nitrate yield a black precipitate of silver peroxide, Ag_2O_2 , this result being, in all probability,

due to the hydrolysis of the silver persulphate formed. When ammonium persulphate is employed instead of the potassium salt, less peroxide is precipitated, but there is, nevertheless, considerable decomposition of the persulphate, as indicated by the formation of sulphate and free sulphuric acid. When ammonia is added to the solution containing ammonium persulphate and the silver salt, there is no deposition of peroxide, but a rapid evolution of the nitrogen produced by the oxidation of ammonia by silver peroxide; in concentrated solutions, the action is very violent and may become uncontrollable. The silver salt acts catalytically, a small amount being sufficient to determine the decomposition of large quantities of persulphate and ammonia in accordance with the following equation: $3(\text{NH}_4)_2\text{S}_2\text{O}_8 + 8\text{NH}_3 = 6(\text{NH}_4)_2\text{SO}_4 + \text{N}_2$.

Ammonium persulphate is slowly decomposed in aqueous solutions containing silver salts without evolving any gas, the change taking place in the following manner: $8(\text{NH}_4)_2\text{S}_2\text{O}_8 + 6\text{H}_2\text{O} = 7(\text{NH}_4)_2\text{SO}_4 + 9\text{H}_2\text{SO}_4 + 2\text{HNO}_3$. A quantitative study of the change shows that for moderate concentrations the rate of decomposition is proportional to the strength of solution.

Considerable quantities of nitric acid are produced on heating concentrated solutions of the persulphate and silver salt, and at the boiling point ozonised oxygen is evolved. The catalytical action of the silver salts on ammonium persulphate gives rise to many interesting cases of oxidation, of which the following may be noted: the bleaching of indigo and methyl-orange, and the oxidation of a chromic salt to chromic acid in an acid solution.

The action of silver compounds has, in addition, an important bearing on the use of ammonium persulphate as a "reducer" in photography. G. T. M.

Electrolysis of Salts in Organic Solvents. By A. W. SPERANSKY and E. G. GOLDBERG (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 797—804).—A number of experiments have been made to find out whether the electrolysis of salts in organic solvents yields the metals in a hard, compact form. Acetone and methyl alcohol solutions of cupric and cobalt chlorides, as well as pyridine solutions of lithium chloride, mercuric iodide, and lead nitrate, did not give good results, as the solutions are either non-conducting or give non-metallic deposits. With a pyridine solution of silver nitrate, aqueous solutions of which yield on hydrolysis dendritic masses of silver, better results are obtained, the silver being deposited in a compact mass firmly attached to the platinum cathode. On passing the same current through aqueous and pyridine solutions of silver nitrate, the latter yields slightly more silver than the former, the mean difference for three experiments being 0.25 per cent; this is probably due to a reducing action exerted by the pyridine on the silver salt. When an anode consisting of equal quantities of silver and copper is employed, the electrolyte being silver nitrate, the silver deposited on the cathode does not contain a trace of copper. In the same way, pure silver is obtained from a pyridine solution of a mixture of silver and lead nitrates, the anode being of lead. Means of separation of silver from copper and from lead are

thus presented. In pyridine solutions of silver nitrate with concentrations of from 3.13 to 13.66 per cent., the salt has a mean molecular weight of 208.8 instead of the theoretical value, 169.55; the molecules are hence, not only non-dissociated, but exist as polymerides, the statement of Werner (Abstr., 1898, ii, 214) that silver nitrate has the normal molecular weight in pyridine being inaccurate. T. H. P.

Borates of Magnesium and the Alkali-earth Metals. By LÉON OUVREARD (*Compt. rend.*, 1901, 132, 257—259).—When magnesium oxide in slight excess is heated to redness with a mixture of boric anhydride and potassium hydrogen fluoride in molecular proportion, the borate $3\text{MgO} \cdot \text{B}_2\text{O}_3$ is obtained in transparent, acicular prisms which show longitudinal extinction; they are not affected by boiling water or acetic acid, but dissolve in inorganic acids. Calcium, barium, and strontium oxides, under the same conditions, yield analogous compounds, which are not affected by cold water, but are decomposed by boiling water and are soluble in acetic acid unless it is very dilute. C. H. B.

Electrolytic Deposition of Lead from Solutions. By L. GLASER (*Zeit. Elektrochem.*, 1900, 7, 365—369 and 381—386).—Homogeneous metallic lead is deposited from slightly acid concentrated solutions of lead nitrate or acetate, containing, preferably, considerable quantities of the corresponding alkali salts, by a current of about 0.004 ampere per sq. cm. at the cathode. When an anode of lead is used, the E.M.F. is about 0.1 volt. When the conditions are such that lead hydroxide can be formed at the cathode, spongy lead is deposited. Concentrated solutions of lead or alkali salts dissolve considerable quantities of lead hydroxide; when such a solution is electrolysed, the removal of lead from the layer of solution in contact with the cathode dilutes it. This more dilute solution deposits the lead hydroxide or basic lead salt which it contains on the cathode, and so prevents the regular deposition of the metal giving rise to the spongy deposit.

Lead chloride and sulphate give unsatisfactory results owing largely to the formation of insoluble lead chloride or peroxide at the lead anode. By using very small current densities and E.M.F.'s, it is, however, possible to obtain coherent deposits.

The deposition of lead may be utilised for plating objects with lead or for separating lead and silver, the alloy being used as anode in a solution of nitrate saturated with chloride; the silver remains behind undissolved.

Coherent deposits of lead are also obtained, although with more difficulty, from alkaline solutions. The concentration of the lead ions is so small in these solutions that the liquid surrounding the cathode soon becomes so impoverished that the E.M.F. rises, and the next available cathion (an alkali metal) is discharged. This results in the secondary reduction of lead sponge. By keeping the E.M.F. low and replacing the liquid in contact with the cathode by vigorous stirring, however, good deposits may be obtained.

The analogy between the deposition of lead and of zinc is pointed out. T. E.

Radio-active Lead. By KARL A. HOFMANN and EDUARD STRAUSS (*Ber.*, 1901, 34, 8—11).—The radio-activity of the "pure lead sulphate," isolated from bröggerite and other minerals (this vol., ii, 19), is enhanced by boiling it with sodium carbonate solution, converting the carbonate so obtained into chloride, and crystallising this from water; the sulphate prepared from the less soluble fractions of the chloride is only feebly radio-active, but that obtained from the more soluble fractions is intensely active. The active sulphate shows a blue fluorescence when exposed to the cathode rays, the radio-activity being thereby increased; its spark spectrum is characterised by a line in the violet. It contains 41.35—42.00 per cent. SO_4 , although lead sulphate should contain only 31.71 per cent.; bismuth sulphate contains 40.86 per cent. SO_4 , but the possibility of bismuth being present is excluded by the method used for purifying the substance. A solution of potassium iodide converts the sulphate into a mass of yellow crystals, which dissolve in warm dilute hydrochloric acid but separate again on heating. On shaking with an excess of potassium iodide containing hydrochloric acid, iodine is liberated. The sulphide and hydroxide prepared from the active sulphate are similar in all respects to the true lead salts; a second sulphate, however, is derivable which contains 22.34 per cent. SO_4 , showing that the metal present is both bivalent and quadrivalent, and probably has an atomic weight of about 260.

On keeping for several months, the radio-activity of the "lead" sulphate diminishes, but can be entirely restored by exposing it to the cathode rays.
W. A. D.

Thallium Chlorobromides of the Type $\text{TlX}_3 \cdot 3\text{TlX}$. By VICTOR THOMAS (*Compt. rend.*, 1901, 132, 80—83).—The yellow product obtained by the action of bromine on thallous chloride in presence of water varies in composition, but when dissolved in water and recrystallised, the first product obtained is always the chlorobromide, $\text{Tl}_4\text{Cl}_3\text{Br}_3$, and this compound is likewise obtained when bromine is added to a warm concentrated solution of thallous chloride.

When the compound $\text{Tl}_3\text{Cl}_2\text{Br}_4$ (this vol., ii, 60) is treated with a large quantity of water, it yields a yellow substance which is similar in appearance to the product of the action of bromine on thallous chloride, and likewise yields the compound $\text{Tl}_4\text{Cl}_3\text{Br}_3$ when recrystallised.

If the chlorobromides $\text{Tl}_4\text{Cl}_4\text{Br}_2$ and $\text{Tl}_4\text{Cl}_2\text{Br}_4$ exist, which is doubtful, they are unstable and decompose when recrystallised, yielding the compound $\text{Tl}_4\text{Cl}_3\text{Br}_3$, which is always formed when thallium, chlorine, and bromine in the form of haloid salts are present together with a sufficient quantity of water. If, however, the solution is concentrated and contains a high proportion of thallic salts, the products seem to belong to the type $\text{TlX}_3 \cdot \text{TlX}$.
C. H. B.

Electrical Deposition of Copper. By J. CAMPBELL DICKSON (*Proc. Phil. Soc. Glasgow*, 1900, 31, 52—65).—The author has studied the way in which the character and amount of the copper deposit from solutions of copper sulphate are affected by alterations in the density of the solutions, and by the presence of acid. Solutions of high

specific gravity give more consistent and trustworthy deposits than solutions of low specific gravity, and the best results are obtained when acid is present. The corrosion of copper plates in copper sulphate has been studied, and the results obtained help to explain the relative behaviour of the solutions just referred to. The author recommends that in the electrolytic deposition of copper from copper sulphate, the solution should have a density of about 1.185, 0.5 per cent. by volume of sulphuric acid should be added, and the current density should be about 60 sq. cm. per ampere. J. C. P.

Reduction of Mercuric Salts by Hydrogen Peroxide. By A. KOLB (*Chem. Zeit.*, 1901, 25, 21).—In the presence of excess of potassium hydroxide or ammonia, mercuric salts are reduced to metal by adding a 3 per cent. solution of hydrogen peroxide and applying heat. In the case of an ammoniacal solution, the reduction is, however, not complete unless a tartrate is present. Even mercuric cyanide may be completely reduced by heating with potassium hydroxide and hydrogen peroxide. Neutral or acid solutions of mercuric salts are not reduced by hydrogen peroxide, but in the presence of sodium potassium tartrate, mercuric chloride is completely reduced to the mercurous state. L. DE K.

Rarefied Gases. By ALBERT COLSON (*Compt. rend.*, 1900, 131, 1202—1204).—Glass tubes of about 50 c.c. capacity containing about 5 grams of red or yellow mercuric oxide were exhausted to a pressure of about $1/200000$ atmosphere and exposed to daylight for a few months. It was then found that a quantity of mercurous oxide and a mirror of mercury had been formed. Examination of the contents showed that 0.6 c.c. of a gas containing 0.2 c.c. of oxygen was present, but analysis proved the loss of oxygen of the mercuric oxide to correspond with over 1.0 c.c. of oxygen, the greater part of which must hence have been removed by some reducing agent emitted from the glass. Other series of experiments were made under different conditions in vacuum tubes and in tubes containing hydrogen; the results are more marked for red than for yellow mercuric oxide, but all confirm the previous result that the glass gives off some reducing agent (compare Trowbridge, *Abstr.*, 1900, ii, 701). L. M. J.

Nona-hydrated Double Iodide of Mercury and Lithium. By D. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 774—779).—From a solution of precipitated mercuric iodide in saturated lithium iodide solution, the double compound of the composition $2\text{LiI}, \text{HgI}_2, 9\text{H}_2\text{O}$, is deposited in the form of soft, waxy, honey-yellow, hygroscopic plates, which float on the mother liquor. T. H. P.

Isolation of Yttria, Ytterbia, and Neo-erbia. By G. and E. URBAIN (*Compt. rend.*, 1901, 132, 136—138. Compare *Abstr.*, 1898, ii, 518; 1900, ii, 346).—The crude rare oxides from gadolinite, converted into ethyl sulphates, yielded after ten crystallisations a mother liquor containing only yttrium, erbium, and ytterbium with a trace of thorium. The soluble ethyl sulphates were converted into nitrates and further fractionation was effected by means of the fusion method; the least basic oxides finally obtained consisted of ytterbia and thoria and these

substances were separated by Wyruboff and Verneuil's process. Gadolinite contains very little thorium, 1 gram being isolated from 25 kilos. of the mineral; the radio-activity of the specimen is identical with that of the element derived from thorite.

The atomic weight of ytterbium is 172.6, that of yttrium is 88.6; their solutions are quite free from absorption bands, and the yttria prepared by the authors does not exhibit the phosphorescent spectrum shown by other specimens; this is probably due to its freedom from gadolinium metals, these elements being readily removed by the ethyl sulphate separation which greatly diminishes the proportion of the intermediate fractions.

G. T. M.

Combination of Aluminium Chloride with Ammonia. By E. BAUD (*Compt. rend.*, 1901, 132, 134—136).—The results of Persoz's investigation (*Ann. Chim. Phys.*, 1830, [ii], 44, 319) on the combination of ammonia and aluminium chloride are not substantiated by the author.

The ammonio-salt $\text{Al}_2\text{Cl}_6 \cdot 12\text{NH}_3$, produced on treating anhydrous aluminium chloride with excess of dry ammonia at the ordinary temperature, is a very stable substance, and far less hygroscopic than the original chloride; when heated at 180° , it loses only 2 mols. of ammonia, forming the compound, $\text{Al}_2\text{Cl}_6 \cdot 10\text{NH}_3$. The latter substance, when heated in a stream of hydrogen, melts at 380° and boils at 450° ; the white, pulverulent salt, $\text{Al}_2\text{Cl}_6 \cdot 2\text{NH}_3$, condensing in the receiver; when the distillation is performed without employing hydrogen, the product has the composition $\text{Al}_2\text{Cl}_6 \cdot 4.61\text{NH}_3$, and consists of a mixture of the di- and deca-ammonio-salts.

At temperatures near the boiling point of ammonia, the deca-ammonio-salt absorbs more of the gas, forming an unstable compound containing 17 or 18 mols. of ammonia.

G. T. M.

Iron and Steel from the Standpoint of the Phase Rule. By HANNS VON JUPTNER (*Chem. Centr.*, 1901, i, 83, 162; from *Stahl. u. Eisen*, 1900, 20, 1205—1212, 1269—1273).—The paper describes the phenomena accompanying the solidification of iron containing carbon, and in so far is on the same lines as Roozeboom's (*Abstr.*, 1900, ii, 728). The author, however, considers the phenomena under the conditions of rapid cooling, in which case the crystals are in equilibrium only with the neighbouring part of the fused mass. For 0.5—2.0 per cent. of carbon, and the temperature interval 1535 — 1130° the author calculates the part of the fused mass which remains liquid when an exchange of carbon between the crystals and the fused mass (1) takes place, (2) does not take place. When all exchange is prevented, a certain portion becomes solid only at the eutectic point. The influence of supercooling is taken into account also.

Roozeboom supposes that at 1000° a saturated solution of carbon in iron contains 1.8 per cent. of carbon; several observations, however, point to the solubility being lower, about 1.5 per cent. It is possible that martensite changes at 690° into ferrite and graphite. Sorbite and troostite are probably transition stages between other forms, and their existence is accordingly due to retardation phenomena.

J. C. P.

Cobalt Peroxide. By THOMAS BAYLEY (*Chem. News*, 1900, **82**, 179—180).—Determinations of the composition of cobalt peroxide by dissolving the washed precipitate in dilute sulphuric acid in the presence of a known excess of ferrous sulphate and subsequent titration with dichromate, indicate that chlorine and bromine in the presence of sodium hydroxide precipitate an oxide of the formula Co_3O_5 at the ordinary temperature, and a lower form at 100° ; the action of hydrogen peroxide is less definite even at the ordinary temperature.

D. A. L.

A New Oxide of Molybdenum: Molybdenum Semipentoxide. By PETER KLASON (*Ber.*, 1901, **34**, 148—153).—When ammonium molybdate is heated with hydrochloric acid containing ammonium iodide (1 mol.) and a small quantity of ammonium chloride until no more iodine is set free, and the residue is then saturated with gaseous hydrogen chloride, *ammonium molybdenyl chloride*, $\text{MoOCl}_3 \cdot 2\text{NH}_4\text{Cl}$, separates in beautiful, green octahedra. It is stable in the air, is not deliquescent, and crystallises from water on saturating with hydrogen chloride; the substance, $3\text{MoCl}_4 \cdot 2\text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$, described by Blomstrand, was probably impure ammonium molybdenyl chloride. On dissolving in water alone it is completely hydrolysed, and, in this state, spontaneously oxidises to molybdenum blue; by alcohol also, it is decomposed, the ammonium chloride being mostly removed. *Molybdenyl hydroxide*, $\text{MoO}(\text{OH})_3$, is precipitated on adding exactly 3 mols. of ammonia to an aqueous solution of the chloride, in a form closely resembling freshly precipitated ferric hydroxide, only brighter in colour; sodium acetate can also be used as a precipitant. It is soluble in water to the extent of 2 parts in 1000, but insoluble in presence of ammonium chloride; it has no acid properties, since it does not dissolve in aqueous alkali hydroxides, and is only slightly soluble in ammonia and alkali carbonates. If in its preparation an excess of ammonia be used, the hydroxide is partially decomposed, and the filtered solution contains much molybdic acid, as stated by Debray; the nature of the precipitate here obtained is being investigated. *Molybdenum semipentoxide*, Mo_2O_5 , obtained by heating the hydroxide in a current of carbon dioxide, is a violet-black powder, soluble in sulphuric and hydrochloric acids to an extent diminishing with the temperature of its formation; it contains traces of molybdic acid which can be removed by alkalis, and also of molybdenum dioxide.

Blomstrand's oxychloride, $2\text{Mo}_3\text{Cl}_{16} \cdot \text{Mo}_3\text{O}_8$, which Püttbach (*Annalen*, 1880, **201**, 123) has considered to be MoOCl_4 , is apparently molybdenyl chloride, since, when dissolved in concentrated hydrochloric acid containing ammonium chloride, it yields the salt, $\text{MoOCl}_3 \cdot 2\text{NH}_4\text{Cl}$.

W. A. D.

The Molybdic Acids. By PETER KLASON (*Ber.*, 1900, **34**, 153—158).—Analyses of ordinary ammonium molybdate agree as well with the formula $5\text{NH}_3 \cdot 6\text{MoO}_3 \cdot 6\text{H}_2\text{O}$ as with Delafontaine's formula, $6\text{NH}_3 \cdot 7\text{MoO}_3 \cdot 7\text{H}_2\text{O}$; determinations of the molecular weight in aqueous solution, taking into account the degree of dissociation indicated by the electrical conductivity, show that it is probably a double salt, $(\text{NH}_4)_3\text{H}_3\text{Mo}_3\text{O}_{12} \cdot (\text{NH}_4)_2\text{H}_4\text{Mo}_3\text{O}_{12}$, which is resolved into its con-

stituents, triammonium and diammonium trimolybdates, when dissolved in water. This view is confirmed by the fact that on adding the calculated quantity of ammonia to the solution, the salt, $(\text{NH}_4)_3\text{H}_3\text{Mo}_3\text{O}_{12}\cdot 4\text{H}_2\text{O}$, separates; this substance was erroneously described by Rammelsberg (*Ann. Phys. Chem.*, 1866, [ii], 127, 298) as $3(\text{NH}_4)_2\text{O}\cdot 7\text{MoO}_3\cdot 12\text{H}_2\text{O}$. Moreover, by adding the calculated quantities of hydrochloric acid, *diammonium trimolybdate*, $(\text{NH}_4)_2\text{H}_4\text{Mo}_3\text{O}_{12}\cdot \text{H}_2\text{O}$, and *ammonium trimolybdate*, $(\text{NH}_4)\text{H}_5\text{Mo}_3\text{O}_{12}$, can be obtained, the former as a granular crust, the latter in slender needles; both salts are decomposed by water, and when dried over phosphoric oxide at the ordinary temperature lose respectively $1\frac{1}{2}$ and $2\text{H}_2\text{O}$; Berlin (*J. pr. Chem.*, 1850, 49, 445) has described the latter salt as $2\text{NH}_3\cdot 4\text{MoO}_3\cdot 3\text{H}_2\text{O}$.

Commercial molybdic acid is really *ammonium anhydrotrimolybdate*, $\text{NH}_3\cdot 3\text{MoO}_3\cdot \frac{1}{2}\text{H}_2\text{O}$. A double salt, $3\text{NH}_3\cdot 6\text{MoO}_3\cdot 5\text{H}_2\text{O}$, intermediate between diammonium and ammonium trimolybdates, was prepared by mixing solutions of these salts and also from ordinary ammonium molybdate by adding the calculated quantity of hydrochloric acid; it forms well-defined, transparent crystals. Svanberg and Struve's salt, $2\text{NH}_3\cdot 2\text{MoO}_3\cdot \text{H}_2\text{O}$, could not be obtained.

Triammonium pentadecamolybdate, $3\text{NH}_3\cdot 15\text{MoO}_3\cdot 20\text{H}_2\text{O}$, prepared by adding either the theoretical or twice the theoretical quantity of hydrochloric acid to a solution of ordinary ammonium molybdate, forms microscopic, six-sided prisms, and can be crystallised by adding it to boiling water and evaporating at the ordinary temperature; if, however, the salt be added to cold water and then warmed, it yields the insoluble *anhydride*, $3\text{NH}_3\cdot 15\text{MoO}_3\cdot 6\text{H}_2\text{O}$. *Triammonium dodecamolybdate*, $3\text{NH}_3\cdot 12\text{MoO}_3\cdot 12\text{H}_2\text{O}$, obtained by adding ammonium chloride to a hot solution of the pentadecamolybdate, crystallises in lustrous aggregates of needles, and is the parent substance of ammonium phosphomolybdate.

W. A. D.

Molybdenum Blue. By PETER KLASON (*Ber.*, 1901, 34, 158—160).—Molybdenum blue does not appear to contain the dioxide, MoO_2 , as hitherto assumed (compare Guichard, *Abstr.*, 1900, ii, 658), but the semipentoxide, Mo_2O_5 , (preceding abstracts). An *insoluble molybdenum blue*, $\text{Mo}_2\text{O}_5\cdot 24\text{MoO}_3\cdot 24\text{H}_2\text{O}$, is formed on exposing an aqueous solution of ammonium molybdenyl chloride to oxidation by air for several months; if the exposure be shorter, a *soluble form*, $\text{Mo}_2\text{O}_5\cdot 18\text{MoO}_3\cdot 21\text{H}_2\text{O}$, is obtained which can be precipitated by adding ammonium chloride. The insoluble substance is, apparently, an analogue of phosphomolybdic acid in which $\text{P}_2\text{O}_5 : \text{MoO}_3 = 1 : 24$.

W. A. D.

Tungsten Arsenide and Chloroarsenide. By EDOUARD DEFACQZ (*Compt. rend.*, 1901, 132, 138—140. Compare *Abstr.*, 1900, ii, 350).—*Tungsten arsenide*, WAs_2 , prepared by heating tungsten hexachloride in a current of hydrogen arsenide from 150° to 350° , is a black, crystalline substance insoluble in water and other solvents, and having a sp. gr 6.9 at 18° . The compound is stable in air at the ordinary temperature, but is readily oxidised at a dull red heat to arsenious and tungstic oxides; hydrogen reduces it completely at 400 — 550° , chlorine under

these conditions yields arsenious chloride and tungsten hexachloride, whilst tungsten disulphide and phosphide are produced by the action of heated sulphur and phosphorus respectively. Hot sulphuric acid attacks the arsenide, evolving sulphur dioxide; hot nitric acid oxidises the substance to tungstic acid. Hydrofluoric and hydrochloric acids have no action on the arsenide, but a mixture of either of these with nitric acid readily dissolves the substance.

Tungsten arsenide is insoluble in aqueous solutions of the alkaline hydroxides, but is readily decomposed by the fused reagents and also by potassium nitrate and carbonate, the final products being alkali arsenates and tungstates. Fused copper reduces the arsenides, yielding metallic tungsten; it was not found possible to produce a subarsenide corresponding with the lower phosphide.

Tungsten chloroarsenide, W_2AsCl_6 , produced by heating a mixture of tungsten hexachloride and liquid hydrogen arsenide in a sealed tube at $60-75^\circ$, is obtained in the form of bluish-black crystals resembling the hexachloride; the substance is hygroscopic and decomposed by water and acids; it is insoluble in the common anhydrous organic solvents, but readily dissolves in aqueous solutions of the alkali hydroxides; dilute nitric acid readily oxidises the substance, yielding a colourless solution and a yellow precipitate of tungstic acid.

G. T. M.

Double Chlorides of Uranyl and the Alkali Metals. Hydrochloride of Uranyl Chloride. By JULES ALOY (*Bull. Soc. Chim.*, 1901, [iii], 25, 153—155).—The double chlorides of uranyl and sodium or potassium are obtained in the anhydrous state, with the composition $UO_2Cl_2 \cdot 2KCl$ and $UO_2Cl_2 \cdot 2NaCl$, by passing dry chlorine successively over heated uranium oxide and the heated alkali chloride. They are golden-yellow compounds which melt at a red heat without decomposition, and are very soluble in water. The chlorides of the alkaline earth metals do not yield analogous compounds under the conditions described.

When a saturated hydrochloric acid solution of uranyl chloride is cooled to -10° , crystals of a very unstable *hydrochloride*,



are obtained.

N. L.

Uranium Nitrate. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1901, 132, 90—91. Compare this vol., ii, 104, 105).—Solutions of uranium nitrate in (I) dilute nitric acid of sp. gr. 1.153, and (II) dilute sulphuric acid of sp. gr. 1.138 have the following sp. gr.:

| Quantity of salt in } 100 parts of acid. } | | 1. | 2. | 3. | 4. | 5. |
|---|-----------|--------------|--------------|--------------|--------------|--------------|
| I { | t° | 11° | 11.8° | 11.3° | 12.0° | 11.6° |
| | Sp. gr. | 1.1585 | 1.1614 | 1.1663 | 1.1698 | 1.1751 |
| II { | t° | 11.2° | 11.8° | 10.7 | 12.0° | 11.4° |
| | Sp. gr. | 1.1427 | 1.1450 | 1.1511 | 1.1540 | 1.1576 |

One part of uranium nitrate dissolves in 23.5 parts of methyl alcohol at $11.2-11.6^\circ$, in 16 parts of ether at $11.9-12.7^\circ$, in 18.4 parts of ethyl acetate at $10.3-10.7^\circ$, and in 5.3 parts of concentrated formic acid at $15.1-15.6^\circ$.

C. H. B.

Uranium Nitrate. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1901, 132, 204. Compare preceding abstract).—Crystallised uranium nitrate, when rapidly calcined, yields a red modification of uranium sesquioxide which seems to be a polymeride of the orange variety; the latter, which is formed by gradually decomposing the nitrate, is partially transformed into the new modification on prolonged heating at a dull red heat. The red polymeride, when heated for 40 hours at a dull red heat or at higher temperatures, is partially converted into a brown oxide; it does not, however, yield the green oxide on heating to redness in a closed platinum crucible.

G. T. M.

Uranium Red. By VOLKMAR KOHLSCHUTTER (*Annalen*, 1901, 314, 311—338).—Uranium red is the name by which Remelé (*Ann. Phys. Chem.*, 1864, [ii], 124, 114; 1865, 125, 209) distinguished the substance obtained by Patera (*J. pr. Chem.*, 1850, 51, 122) on precipitating uranium nitrate or chloride with ammoniacal hydrogen sulphide, and allowing the product to change spontaneously. The author has subjected this compound to a close investigation, the results of which may be summarised as follows. (1) Alkaline, neutral, and even slightly acid solutions of uranic acid are reduced by hydrogen sulphide. (2) In presence of alkali, the reduction may be retarded if the action of hydrogen sulphide on the alkali uranate takes place in a solution containing excess of uranyl sulphate or nitrate. (3) Under these conditions, an orange-yellow compound is produced, yielding the blood-red substance, "uranium red," when treated with alkali. (4) Uranium red contains uranium, sulphur, and alkali metal in the proportion 5 : 2 : 5. (5) All the uranium is present as trioxide. (6) One of the alkali atoms is more loosely combined than the others. When this is removed, the yellow, intermediate compound is produced; it is feebly acid, and contains uranium, sulphur, and alkali in the proportion 5 : 2 : 4. (7) Treatment with dilute hydrochloric acid eliminates one-half the sulphur from this compound in the form of hydrogen sulphide, and the remainder as the free element; this suggests that uranium red contains a disulphide residue which acts as the carrier of the loosely attached alkali atom. (8) In the uranium alkali residue, $5\text{UO}_3 \cdot 2\text{R}_2\text{O}$, the four alkali atoms may be replaced by the alkaline earths without altering the chemical character of the compound; the five molecules of uranic acid are therefore grouped in one complex, which takes part, as such, in reactions.

In the author's opinion, the formulæ, $\text{HS} \cdot \text{S} \cdot \text{U}(\text{OH})(\text{O} \cdot \text{UO}_2 \cdot \text{OR})_4$ and $\text{RS} \cdot \text{S} \cdot \text{U}(\text{OH})(\text{O} \cdot \text{UO}_2 \cdot \text{OR})_4$, represent the yellow, parent compound and uranium red respectively.

M. O. F.

Action of Hydrogen on Bismuth Monosulphide. By HENRI PÉLABON (*Compt. rend.*, 1901, 132, 78—80).—The author has investigated the action of hydrogen on various masses of bismuth monosulphide, and on mixtures of the monosulphide and bismuth, and the action of hydrogen sulphide on bismuth, with a view to determine the conditions of equilibrium. With hydrogen and bismuth sulphide at 610° , if R is the ratio of the weight of the unaltered sulphide to the total weight of the unaltered sulphide and the reduced bismuth, and ρ

is the ratio of the mass of hydrogen sulphide to the total mass of the gas, it is found when R increases from 0.89 and tends towards 1, ρ remains practically constant at about 0.893.

With hydrogen sulphide and bismuth, ρ tends regularly towards zero as R tends to zero, and when the weight of bismuth in a tube of 6 c.c. capacity exceeds 1 gram, ρ is practically proportional to R .

With hydrogen and a mixture of bismuth and bismuth sulphide, ρ increases very regularly as R increases. At 610°, equilibrium is attained in about 20 minutes, and it is immaterial whether the bismuth and bismuth sulphide are mixed or are kept in different parts of the tube.

When the temperature is between the melting points of bismuth and bismuth sulphide, the value of ρ for a given value of R is not the same when hydrogen sulphite acts on bismuth as when hydrogen acts on bismuth sulphide. In the former case, the film of bismuth sulphide formed on the surface of the metal interferes with the reaction, in the latter, the value of ρ at 440° is independent of the mass of bismuth sulphide, as the theory of dissociation indicates in the case of partially heterogeneous systems.

C. H. B.

Mineralogical Chemistry.

Colours of Minerals. By K. VON KRAATZ-KOSCHLAU and LOTHAR WÖHLER (*Zeit. Kryst. Min.*, 1900, **33**, 632—636; from *Tsch. Min. Mitth.*, 1899, **18**, 304—333, 447—468).—When certain minerals are ignited, the loss of colour is accompanied by a smell of burning organic matter and the production of carbon dioxide, together with, in many cases, a phosphorescence of the mineral lasting only so long as the colour and smell are observable. On these grounds, it is considered that the following minerals may be coloured by organic matter: fluor, apatite, barytes, celestite, anhydrite, salt, calcite, zircon, smoky quartz, amethyst, amazon stone, rubellite and topaz. Several determinations are given of the amount of carbon and hydrogen present; the following may be selected as examples for different minerals:

| | C. | H per cent. |
|--|--------|-------------|
| Fluor (blue and green) from Cumberland | 0·009 | 0·002 |
| Anhydrite | 0·02 | 0·011 |
| Zircon from Arendal | 0·016 | 0·013 |
| Smoky quartz | 0·04 | 0·0073 |
| Amethyst..... | 0·009 | 0·005 |
| Amazon stone | 0·05 | 0·0145 |
| Topaz from Brazil | 0·0076 | 0·0098 |

The small amounts of ammonia obtained on heating zircon and smoky quartz are probably derived from organic substances.

Colours which are not destroyed by heat must be due to inorganic substances; those possibly due to chromium, titanium, nickel, manganese

and iron are considered. The colour of melanite and of black anatase appears to be due to titanium sesquioxide (Ti_2O_3). L. J. S.

Colour of Zircon. By GIORGIO SPEZIA (*Zeit. Kryst. Min.*, 1900, 33, 636; from *Atti R. Accad. Sci. Torino*, 1899, 34, 638—642. Compare preceding abstract).—The author long ago stated that the red colour of zircon from Ceylon is due to the presence of ferric oxide. Recent experiments support this view, and prove that Kraatz and Wohler's view is incorrect. The loss in colour on heating is explained by the reduction of ferric oxide by organic matter. L. J. S.

Colouring Matter of Smoky Quartz. By J. KOENIGSBERGER (*Zeit. Kryst. Min.*, 1900, 33, 637; from *Tsch. Min. Mitth.*, 1899, 19, 148—154. Compare preceding abstracts).—The conclusions of Kraatz and Wöhler are adversely criticised, and their observations are carefully repeated for rose fluor and smoky quartz. After allowing for various sources of error, the amounts of carbon and hydrogen determined are only about one-tenth of those found by Kraatz, and even these are probably too high. Kraatz and Wöhler's statement that smoky quartz contains no titanium is confirmed; the colour cannot therefore be due to the presence of titanium sesquioxide as suggested by Weinschenk (*Abstr.*, 1896, ii, 654). L. J. S.

Colours of Minerals. By ERNST WEINSCHENK (*Zeit. Kryst. Min.*, 1900, 33, 638; from *Tsch. Min. Mitth.*, 1899, 19, 144—147. Compare preceding abstracts).—Arguments are given against the supposition that the colours of certain minerals are due to organic matter (compare *Abstr.*, 1896, ii, 654). L. J. S.

Native Tellurium from Hannan's District, Western Australia. By R. W. EMERSON MACIVOR (*Chem. News*, 1900, 82, 272).—Tellurium has been found associated with pyrites from Hannan's district, Western Australia; it has a finely-granular, white, metallic appearance. Analysis gave:

| Te. | Au. | Total. |
|--------|-------|--------|
| 96.935 | 2.399 | 99.334 |

D. A. L.

Alteration of Pyrites by Underground Water. By JOHN WILLIAM EVANS (*Min. Mag.*, 1900, 12, 371—377).—Water containing oxygen and calcium carbonate may act on pyrites in accordance with the following equation: $4FeS_2 + 15O_2 + 3H_2O + 8CaCO_3 = (Fe_2O_3)_2(H_2O)_3 + 8CaSO_4 + 8CO_2$. Here there is no loss of iron, and the molecular volume of the resulting limonite is almost exactly equal to that of the original pyrites. From this it is concluded that the solidity of rocks containing much pyrites will not be affected by underground waters containing a sufficient amount of calcium carbonate in proportion to free oxygen. When distilled water is allowed to drop onto pyrites, ferrous sulphate and sulphuric acid are formed, but the pyrites remains bright even after several months. With ordinary river water containing calcium carbonate, limonite and gypsum are formed as indicated by the above equation. Similar results were obtained with marcasite, zinc-blende, and copper-

pyrites. Arsenides (niccolite &c.) are altered to arsenates when allowed to remain in distilled water, but in this case the presence of calcium carbonate seems to retard the action.

L. J. S.

Conchite, a New Form of Calcium Carbonate. By AGNES KELLY (*Sitzungsber. Akad. München*, 1900, 187—194; *Min. Mag.*, 1900, 12, 363—370).—A description is given of a new form of calcium carbonate, which is optically uniaxial and negative, but with refractive indices different from calcite, and no cleavage or twinning. Sp. gr. 2.87. It occurs as various animal secretions (for example, those of molluscs, &c., formerly supposed to consist of aragonite), the “fur” of kettles, and in the hot springs of Carlsbad, Bohemia (compare ktypeite, Abstr., 1898, ii, 604). It crystallises from hot solutions, whilst calcite crystallises from cold solutions. At a temperature of 300—310°, it is altered into calcite, whilst the change of aragonite to calcite takes place at 405°.

The shell of *Cardium edule* consisting of conchite was found to contain CaO, 54.63; CO₂, 42.45 = 97.08, the difference being organic matter and a possible trace of sodium chloride. In the shell of *Cyrena*, the amount of CaO corresponds to 97.2 per cent. CaCO₃.

An amorphous form of calcium carbonate is also described.

L. J. S.

Artificial Preparation of Polyhalite. By E. E. BASCH (*Sitzungsber. Akad. Wiss. Berlin*, 1900, 48, 1084).—Polyhalite has been artificially prepared in two ways. In the first, syngenite and epsomite were placed in a solution containing sodium, potassium and magnesium chlorides and magnesium sulphate, and heated at 56° for some hours, when the syngenite is converted into polyhalite, [Ca₂K₂Mg(SO₄)₄·2H₂O]. In the other method, potassium sulphate dissolved in water is shaken with gypsum, the resulting paste of syngenite is mixed with crystalline magnesium sulphate and chloride, and kept at 56° until sufficient water has been lost by evaporation; the mixture is then filtered and the precipitate washed with alcohol.

R. H. P.

A Rhombic Pyroxene from South Africa. By HERRERT LISTER BOWMAN (*Min. Mag.*, 1900, 12, 349—353).—Determinations are given of the characters of some clear, transparent, irregular fragments of a bright green colour from the diamond washings of South Africa. There is a perfect prismatic cleavage with an angle of 88°0'; less perfect cleavages are *a*(100) and *b*(010). Sp. gr. 3.199. The optical characters and the following approximate analysis point to the mineral being enstatite:

| SiO ₂ . | FeO. | MnO. | Al ₂ O ₃ . | Cr ₂ O ₃ . | MgO. | Total. |
|--------------------|------|------|----------------------------------|----------------------------------|------|--------|
| 56.0 | 5.0 | 0.5 | 2.5 | 0.6 | 36.5 | 101.1 |

L. J. S.

[**Mineral Analyses.**] By HAROLD W. FAIRBANKS (*Zeit. Kryst. Min.*, 1900, 33, 658; from *Bull. Dept. Geol. Univ. California*, 1896, 2, 1—92. Compare Abstr., 1897, ii, 55).—In a geological paper, the following analyses are given of augite (I), feldspar (II), and analcite

(III) from an augite-teschenite from Point Sal, Santa Barbara Co., California.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | CaO. | MgO. | K ₂ O. | Na ₂ O. |
|------|--------------------|----------------------------------|----------------------------------|------|-----------|-------|-------------------|--------------------|
| I. | 46.59 | 9.69 | 1.03 | 4.75 | 21.38 | 13.89 | 1.23 | |
| II. | 52.72 | 30.46 | — | — | 11.01 | — | 0.42 | 3.70 |
| III. | 54.40 | 23.04 | — | — | 0.21 | — | 0.19 | 13.33 |
| | Ignition. | | Total. | | Sp. gr. | | | |
| | I. | | 1.22 | | 99.78 | | | |
| | II. | | 1.44 | | 2.338 | | | |
| | III. | | 8.46 | | 2.63—2.67 | | | |
| | | | | | 2.261 | | | |

L. J. S.

Mode of Occurrence of Topaz near Ouro Preto, Brazil. By ORVILLE A. DERBY (*Amer. J. Sci.*, 1901, [iv], 11, 25—34).—The statement that the topaz of Ouro Preto occurs in talcose or chlorite-schist is incorrect. It occurs, usually in nodules, in a clayey matrix which has resulted from the decomposition of a mica-schist, the latter having probably been derived from an eruptive rock of the augite- or nepheline-syenite groups, in which the topaz was crystallised in drusy cavities. Associated minerals are rutile, tourmaline, euclase, florencite (Abstr., 1900, ii, 601), &c.

L. J. S.

Albite from Amelia, Virginia. By FRANZ ERBEN and L. CEIPEK (*Tsch. Min. Mitth.*, 1901, 20, 85).—The following analysis is of rather cloudy cleavage fragments of albite, which has been examined optically by F. Becke (*ibid.*, 19, 321). Formula, $Ab_{19}An_1$:

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | MnO. | CaO. | MgO. | K ₂ O. | Na ₂ O. | Li ₂ O. | Total. |
|--------------------|----------------------------------|----------------------------------|-------|------|------|-------------------|--------------------|--------------------|--------|
| 68.96 | 20.26 | 0.23 | trace | 1.05 | 0.22 | 0.11 | 9.89 | trace | 100.72 |

L. J. S.

Constitution of Andalusite and of Disthene. By KARL ZULKOWSKI (*Monatsh.*, 1900, 21, 1086—1094. Compare Abstr., 1900, ii, 595).—When these two minerals are heated with a large excess of potassium carbonate until constant in weight, the loss of carbon dioxide in each case indicates that 1.5 molecules of alkali become united with the mineral (SiO_2, Al_2O_3). These results do not agree with Groth's views on the molecular structure of the two minerals and necessitate the doubling of the molecular formulæ to $2SiO_2, 2Al_2O_3$.

J. J. S.

[**Mineral Analyses.**] By WALDEMAR CHRISTOFER BRÖGGER (*Skrifter Vid.-Selsk. Christiania, Math.-natur. Kl.*, 1898 (1897), No. 6, 90—100).—The following mineral analyses by V. Schmelck are given in a petrological paper (pp. 1—377) describing the dyke-rocks in the Christiania district. Heumite is the name given to a dyke-rock from Heum, consisting of hornblende and felspar, with some biotite, and smaller amounts of nephelite, sodalite, diopside, &c. The hornblende (anal. I; also fluorine 0.31; 1.51 per cent. of apatite has been deducted) is intermediate between basaltic hornblende and barkevikite, but nearer the former; sp. gr. 3.2—3.3. The felspar consists mainly of anorthoclase of sp. gr. 2.62—2.64 (anal. II); after deducting 3.09 per

cent. of hornblende and 7.00 per cent. of nephelite, the composition of the pure anorthoclase is given under III. The bulk analysis of the rock gave the results under IV (also P_2O_5 , 0.48 per cent.). Hornblende from Brandberget, consisting essentially of hornblende, gave the results under V, and is thus very similar in composition to the hornblende under I. Numerous other rock analyses are given in the paper :

| | SiO ₂ . | TiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | CaO. | MgO. |
|------|--------------------|--------------------|----------------------------------|----------------------------------|------|------|-------|------|
| I. | 40.29 | 4.37 | 10.93 | 7.84 | 9.70 | 0.15 | 11.83 | 9.78 |
| II. | 62.32 | — | 21.90 | 0.51 | — | — | 2.52 | 0.32 |
| III. | 65.59 | — | 21.37 | — | — | — | 2.29 | — |
| IV. | 47.10 | 1.75 | 16.42 | 4.63 | 7.04 | 0.36 | 7.64 | 5.00 |
| V. | 37.90 | 5.30 | 13.17 | 8.83 | 8.37 | — | 10.75 | 9.50 |

| | K ₂ O. | Na ₂ O. | Loss on ignition. | Total. |
|------|-------------------|--------------------|-------------------|--------|
| I. | 1.61 | 3.19 | — | 100.00 |
| II. | 1.19 | 9.97 | 1.59 | 99.32 |
| III. | 0.90 | 9.85 | — | 100.00 |
| IV. | 3.47 | 6.36 | 0.40 | 100.65 |
| V. | 2.12 | 2.35 | 1.40 | 99.69 |

L. J. S.

Analyses of Rock-forming Minerals from the Tatra Mountains. By L. GORAZDOWSKI (*Zeit. Kryst. Min.*, 1900, 33, 656—658; from *Pamiętnik. Fizyograficzny*, 1898, 15).—Muscovite from various granites gave analyses I—III, that from gneiss gave IV; measurements of the optic axial angle are given. Biotite from granite gave V, and from biotite-garnet-schist VI. Garnet from the last rock gave VII. Red porphyritic crystals of orthoclase, and greenish albite from the ground-mass of a granite, gave VIII and IX respectively. Hornblende from a diorite gave X, and from an amphibolite XI :

| | SiO ₂ . | TiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | CaO. | MgO. | K ₂ O. | Na ₂ O. | H ₂ O. | Total. |
|-------|--------------------|--------------------|----------------------------------|----------------------------------|-------|------|-------|-------|-------------------|--------------------|-------------------|--------|
| I. | 38.85 | 3.94 | 30.64 | 2.03 | — | — | 0.69 | trace | 9.50 | 1.70 | 13.27 | 100.63 |
| II. | 45.36 | 2.70 | 28.35 | 2.60 | — | — | 0.18 | trace | 9.23 | 1.89 | 9.99 | 100.30 |
| III. | 42.27 | 2.66* | 31.57 | 2.63 | — | — | 1.06 | 0.86 | 10.05 | 3.49 | 6.07 | 100.68 |
| IV. | 41.27 | 1.67 | 33.94 | 0.95 | — | — | 0.29 | trace | 9.98 | 2.43 | 9.39 | 99.92 |
| V. | 34.53 | 2.26 | 19.88 | 7.50 | 14.16 | — | 0.26 | 5.01 | 7.55 | 0.82 | 6.03 | 98.00 |
| VI. | 35.12 | 2.04 | 19.52 | 8.08 | 15.69 | — | 0.47 | 4.77 | 7.25 | 0.84 | 6.33 | 100.11 |
| VII. | 34.41 | 1.01 | 20.34 | 34.33 | | 5.72 | 1.84 | 1.80 | — | — | 0.55 | 100.00 |
| VIII. | 63.91 | — | 17.71 | trace | | — | 0.33 | — | 13.22 | 3.10 | 0.68 | 98.95 |
| IX. | 65.23 | — | 19.18 | trace | | — | 1.81 | trace | 2.16 | 7.94 | 2.10 | 98.42 |
| X. | 46.39 | — | 8.11 | 4.64 | 9.68 | — | 14.17 | 11.82 | 0.63 | 0.82 | 2.30 | 98.56 |
| XI. | 44.86 | — | 11.94 | 8.85 | 12.34 | — | 10.70 | 7.68 | 0.99 | 1.16 | 1.84 | 100.36 |

L. J. S.

Microperthite from Wisconsin. By SAMUEL WEIDMANN (*Zeit. Kryst. Min.*, 1900, 33, 658; from *Bull. Wisconsin Geol. and Nat. Hist. Survey*, 1898, 3).—In a geological paper on the pre-Cambrian igneous rocks of the Fox River Valley, Wisconsin, the following analysis by Tolman is given of microperthite which occurs as a constituent of rhyolite. It consists of albite and oligoclase-andesine with extinction

* Including ZrO₂.

angles on (010) of 19° and $5-7^\circ$ respectively; these have probably been derived by the alteration of a single plagioclase.

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | K ₂ O. | Na ₂ O. | Total. |
|--------------------|----------------------------------|----------------------------------|------|-------------------|--------------------|--------|
| 62.57 | 18.12 | 1.32 | 5.52 | 5.11 | 7.20 | 99.84 |
| L. J. S. | | | | | | |

Gaseous Products Liberated by the Action of Heat on some Igneous Rocks. By ARMAND GAUTIER (*Compt. rend.*, 1901, 132, 58—65).—Igneous rocks such as granite, porphyry, ophite, and lherzolite, when heated at about 1000° in a vacuum, yield from 2500 c.c. to 5500 c.c. of gas per kilogram, in addition to from 7 to 17 grams of water. The gas consists chiefly of hydrogen, carbon dioxide, and carbon monoxide, with some methane, and except in the case of porphyry, some hydrogen sulphide. In the case of lherzolite, carbon dioxide is the chief constituent, and the proportion of hydrogen sulphide is more than half as high again as the proportion of hydrogen. The total volume of water vapour and gas emitted by these rocks at 1000° is not less than 100 times the volume of the rock itself, and this fact has an important bearing on volcanic action. C. H. B.

Production of Hydrogen in Igneous Rocks. Action of Steam on Ferrous Salts. By ARMAND GAUTIER (*Compt. rend.*, 1901, 132, 189—194).—A study of the action of heated chalybite on carbon dioxide or steam confirms the results obtained by Tilden (*Abstr.*, 1898, ii, 383). Owing to the presence of traces of sulphides and nitrogenous compounds in the mineral employed, the gaseous product contained small quantities of hydrogen sulphide and ammonia. Ferrous sulphide free from iron, is transformed by steam into the magnetic oxide of iron, the gases evolved consisting of a mixture of hydrogen and hydrogen sulphide.

Analogous results are obtained with ferruginous siliceous rocks (porphyrites and granites); these mineral specimens contain water which is evolved only at a red heat, and at this temperature acts on the ferrous compounds yielding hydrogen. A specimen of ophitic rock, maintained at red heat until its gaseous constituents are entirely removed, was made to yield fresh quantities of gas by heating it in a current of steam; in this case, the product was a mixture of methane, nitrogen, hydrogen, and the oxides of carbon. G. T. M.

Ceylon Rocks and Graphite. By ANANDA K. COOMARA-SWAMY (*Quart. J. Geol. Soc.*, 1900, 56, 590—614. Compare *Abstr.*, 1899, ii, 500).—With the exception of recent deposits (gem-gravels, &c.), Ceylon is probably entirely composed of ancient crystalline rocks, mainly granulites, in which veins of graphite often occur. The following analyses of rock-forming minerals by S. Hastings and Shepherd are given. Hypersthene from a quartz-norite gave the results under I (mean of two duplicate analyses which, however, differ considerably). Pale-greenish mica (anal. II; also F, 0.78, traces of Fe₂O₃ and organic matter), with the optical characters of biotite, occurs with sky-blue apatite and sahlite in a crystalline limestone. Some rocks from Galle are peculiar in being composed of scapolite, wollas-

tonite in large ophitic plates (analyses III and IV), quartz, a pale green pyroxene (shown by anal. V to be manganhedenbergite), &c.

| | SiO ₂ | Al ₂ O ₃ | FeO. | MnO. | CaO. | MgO. | K ₂ O. | Loss on ignition. | Total. | Sp. gr. |
|------|------------------|--------------------------------|-------|------|-------|-------|-------------------|----------------------|--------|---------|
| I. | 50.45 | 0.72 | 28.41 | — | — | 21.05 | — | — | 100.63 | 3.55 |
| II. | 40.72 | 26.38 | — | — | — | 14.27 | 10.36 | 7.63 | 99.81 | 2.57 |
| III. | 51.28 | 2.01 | 1.34 | — | 45.55 | — | — | not est. | 100.18 | 2.76 |
| IV. | 54.59 | 1.77 | 0.70 | — | 40.85 | — | — | 2.29 | 100.20 | 2.78 |
| V. | 50.91 | 1.78 | 19.91 | 2.64 | 24.41 | 0.58 | — | — | 100.23 | 3.377 |

L. J. S.

Chemical Study of the Glaucophane-Schists. By HENRY S. WASHINGTON (*Amer. J. Sci.*, 1901, [iv], 11, 35—59).—A review is given of the literature of several occurrences of glaucophane-schists, and many new analyses and petrological descriptions are added. These rocks may be divided into two main groups, a basic and an acid; the former are composed chiefly of glaucophane and epidote, and have been derived by the regional or contact metamorphism of igneous rocks of the gabbro family; those of the rarer acid division are composed mainly of quartz and glaucophane with mica, and have been derived from sedimentary rocks. The following analysis is given of glaucophane, sp. gr. 3.11, isolated from a quartz-mica-glaucophane-schist from the island of Syria, Greece:

| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | FeO. | MnO. | CaO. | MgO. | Na ₂ O. | K ₂ O. | H ₂ O. | Total. |
|------------------|--------------------------------|--------------------------------|------|------|------|------|--------------------|-------------------|-------------------|--------|
| 57.67 | 11.07 | 3.20 | 9.68 | 0.06 | 0.95 | 9.85 | 6.80 | 0.42 | 0.48 | 100.18 |

L. J. S.

[**Fassaite from Syria.**] By L. FINCKH (*Zeit. Kryst. Min.*, 1900, 33, 651; from *Zeit. Deutsch. geol. Ges.*, 1898, 50, 79—146).—The gabbros and serpentines of northern Syria are described. A fassaite-fels occurs as a contact product of serpentine in the Kurden mountains. Pure cleavage flakes of fassaite gave the following results on analysis; the angle of optical extinction on (010) is 30°, and there is a diallage-like parting parallel (100):

| SiO ₂ | Al ₂ O ₃ | FeO. | CaO. | MgO. | Ignition. | Total. |
|------------------|--------------------------------|------|-------|------|-----------|--------|
| 48.72 | 18.50 | 3.05 | 20.89 | 6.82 | 2.23 | 100.21 |

L. J. S.

Analysis of the Kesen Meteorite. By JOHN M. DAVISON (*Chem. Centr.*, 1901, i, 274; from *Proc. Rochester Acad. Sci.*, 1900, 3, 201—202).—I, the portion (31.68 per cent.) soluble in hydrochloric acid. II, the insoluble portion (51.79 per cent.). III, the metallic portion attracted by a magnet (16.53 per cent.). IV, the composition of the whole:

| | SiO ₂ | Fe ₂ O ₃ | Al ₂ O ₃ | CaO. | MgO. | Na ₂ O. | K ₂ O. |
|------|------------------|--------------------------------|--------------------------------|------|-------|--------------------|-------------------|
| I. | 7.35 | 45.32 | 1.63 | 1.68 | 41.58 | — | — |
| II. | 64.15 | 6.97 | 5.35 | 3.49 | 17.80 | 1.27 | 0.05 |
| III. | — | — | — | — | — | — | — |
| IV. | 36.24 | 18.04 | 3.34 | 2.35 | 22.54 | 0.34 | 0.01 |

| | P ₂ O ₅ . | S. | Fe. | Ni. | Co. | Total. |
|------|---------------------------------|------|-------|-------|------|--------|
| I. | 0·10 | 0·19 | — | 2·00 | 0·17 | 99·92† |
| II. | — | — | — | — | — | 99·08 |
| III. | 0·12* | 1·56 | 87·22 | 10·05 | 0·46 | 99·41 |
| IV. | 0·36 | 1·53 | 13·00 | 2·13 | 0·12 | 100·00 |

* Phosphorus.

† Less 0·10 O for S.

L. J. S.

Chemical Investigations in the Red Sea. By KONRAD NATTERER (*Monatsh.*, 1900, 21, 1037—1060).—Detailed analyses are given of samples of water and soil, and soundings from the sea bed collected during a voyage of the *Pola* in the southern half of the Red Sea during 1897 and 1898 (compare Abstr., 1899, ii, 501). The waters were examined as to specific gravity and amount of organic matter; the specimens from the sea bed were analysed mainly for magnesium and calcium carbonates.

J. J. S.

Physiological Chemistry.

Capacity of Man to Adapt Himself to High and Low Temperatures. By MAX RUBNER (*Arch. Hygiene*, 1900, 38, 120—147).—A large number of observations are recorded on human beings at different temperatures of the surrounding air, with and without clothing. The most striking result is the comparative constancy of the gaseous exchanges in the lung; the main adaptation to the altered surroundings is carried out by the skin in the loss of water.

W. D. H.

Skin Activity in Europeans and Negroes. By MAX RUBNER (*Arch. Hygiene*, 1900, 38, 148—159).—Apart from considerations of diet, which are treated of especially in relation to its heat value in warm climates, the principal point made in the paper as the result of observations on skin activity in negroes and Europeans is that but little difference is observable in the two classes. Observations at different temperatures of the surrounding air and with different kinds of clothing are recorded.

W. D. H.

Chemical Composition of New-born Children. By WILLIAM CAMERER, jun., and FRIEDRICH SÖLDNER (*Zeit. Biol.*, 1900, 40, 529—534).—Further experiments to show that the ash of milk and of the offspring do not correspond as Bunge states. Besides the ash, quantitative experiments are given to show the proportion of the various organic constituents in new-born children. The main results are as follows:

| | Water. | Fat. | Ash. | Proteid and gelatin. | Extrac- tives. | C. | H. | N. |
|------------------------|--------|------|------|----------------------------|-------------------|------|-----|-----|
| Two male children ... | 71 | 13 | 2·7 | 12 | 1·2 | 16·6 | 2·4 | 2·0 |
| Two female children... | 72 | 12 | 2·6 | 11 | 1·6 | 15·6 | 2·3 | 1·9 |

W. D. H.

Composition of the Ash of Milk and of the New-born Child. By CORNELIA DE LANGE (*Zeit. Biol.*, 1900, 40, 526—528).—The correspondence of the composition of the ash of milk and offspring described by Bunge is not altogether supported by the results obtained by Hugouenq (Abstr., 1899, ii, 503, 682), and of Camerer and Söldner (Abstr., 1900, ii, 290). In the present investigation, the methods of Camerer and Söldner were used; human milk and a still-born infant were the subjects of the experiments. It will be seen in the following table that the numbers, which are percentages of the ash obtained, differ considerably from those of Camerer and Söldner:

| | Ash of infant. | | Ash of human milk. | |
|--------------------------------------|-------------------|----------|--------------------|----------|
| | Present research. | Söldner. | Present research. | Söldner. |
| K ₂ O | 6.5 | 7.8 | 19.9 | 31.4 |
| Na ₂ O | 8.8 | 9.1 | 29.6 | 11.9 |
| CaO | 38.9 | 36.1 | 12.9 | 16.4 |
| MgO | 1.4 | 0.9 | 2.9 | 2.6 |
| Fe ₂ O ₃ | 1.7 | 0.8 | 0.25 | 0.16 |
| P ₂ O ₅ | 37.6 | 38.9 | 17.9 | 13.5 |
| Cl ₂ | 6.3 | 7.7 | 21.3 | 20.0 |

W. D. H.

[Obesity in Relation to Respiration]. By ARTHUR SCHATTEN-FROH (*Arch. Hygiene*, 1900, 38, 93—113).—The observations relate principally to loss of water by the skin. They show that at rest the loss of water per square unit of the body, as the temperature of the air is raised, is about 40 per cent. greater than for thin people. The difference is much more marked during work.

W. D. H.

Cause of Apnœa. By LÉON FREDERICQ (*Bull. Acad. Roy. Belg.*, 1900, 464—482).—Much discussion has occurred in relation to the question whether apnœa is of nervous or chemical origin. The present results are in favour of the latter view. Experiments in crossed cerebral circulation show there is true chemical apnœa, but the increase in oxygen tension of the blood is so slight that this cannot be the cause of the phenomenon. Moreover, the tension can be increased threefold without producing apnœa. It is rather to be attributed to decrease in carbon dioxide, the amount of which sinks to less than half the normal. Intravascular injections of sodium hydroxide do not increase markedly the alkalinity of the blood in the dog. Such injections do not diminish the tension of carbon dioxide, and apnœa does not result.

W. D. H.

The Toxicity of Expired Air. By EMMANUEL FORMÁNEK (*Arch. Hygiene*, 1900, 38, 1—66).—An elaborate research, with references to former work, especially that of Brown-Séquard and D'Arsonval, who are mainly responsible for a prevalent opinion that expired air contains certain specific poisonous substances, possibly of an alkaloidal nature. The present research shows that ammonia can frequently be detected in the expired air, but this is not added to the air in the lungs, but in the mouth, as the result of putrefactive changes, especially in carious teeth. No specific poison exists in the true expired air except carbon dioxide.

W. D. H.

NOTE.—No reference is made to the work of Haldane and Smith (Abstr., 1892, 1502 ; 1893, ii, 223), who obtained the same result.

W. D. H.

Permeability of the Red Blood Corpuscles for $\overline{\text{NO}}_3$ and $\overline{\text{SO}}_4$ Ions. By HARTOG J. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 371—374).—If red blood corpuscles previously treated with carbon dioxide in dextrose solution are placed in a solution of sodium chloride, the latter becomes alkaline, owing to the $\overline{\text{CO}}_3$ ions passing out of the cells and replacing the $\overline{\text{Cl}}$ ions. For every $\overline{\text{CO}}_3$ ion that leaves a cell two $\overline{\text{Cl}}$ ions enter it, so that the corpuscle swells. On similar grounds, the author concludes that the red blood corpuscles are permeable for $\overline{\text{NO}}_3$ and $\overline{\text{SO}}_4$ ions.

J. C. P.

Calcium and Sodium Citrates in the Coagulation of the Blood, Lymph, and Milk. By LUIGI SABBATANI (*Atti R. Accad. Sci. Torino*, 1901, 36, 27—53).—Experiments have been made on the action of normal sodium citrate in rendering blood non-coagulable, and it is found that to bring about this condition in blood which has been removed from the body of the animal, 3 mol. of the sodium citrate are required for each atom of calcium contained in the blood. When the citrate is intravenously injected, however, the necessary proportion is raised to about five times the above, from which it is concluded that in this case the citrate not only acts on the soluble calcium salts in the blood, but diffuses into the tissues and fixes the calcium salts found both there and in the other liquids of the organism. Blood which has been rendered non-coagulable owing to the presence of sodium citrate is again made coagulable by the addition of calcium salts, the quantity of calcium required to bring about this result increasing with the amount of citrate present. Similar considerations hold for the coagulability of lymph and of milk, the results in the latter case supporting Vaudin's hypothesis that the citric acid normally present in milk assists in maintaining in solution the calcium salts contained therein. Further, the experiments lend confirmation to the view that the presence of calcium is indispensable for the coagulation of blood, lymph, and milk, and show also that the calcium must be present in a chemically active condition, that is, in the form of ions.

T. H. P.

Mechanism of the Actions of Diastases. By MAURICE HANRIOT (*Compt. rend.*, 1901, 132, 212—215. Compare Abstr., 1897, ii, 378).—The hydrolysis of glyceryl esters by the lipase contained in the serum of the horse is an action which is arrested by the presence of excess of acid, but not by that of glycerol ; this fact confirms the view that the reaction is due to the formation of an unstable compound of the acid with the enzyme.

The hydrolytic action appears to be a balanced reaction, and the inverse change is effected when a solution containing 5 parts of glycerol, 2 parts of butyric acid, and an excess of neutralised serum is maintained at 37°, the loss of acidity being 54 per cent. in 1½ hours.

Under these conditions the acidity of a solution of glycerol and butyric acid containing no serum remains constant, and this is also the case when the serum has been previously boiled, or when it is added to a solution which is free from butyric acid.

The lipase also promotes the esterification of the mineral acids; in the case of the acids of the acetic series, the amount of combination increases with the molecular weight of the acid. G. T. M.

Physiology of Glands. By LEON ASHER and WILLIAM D. CUTTER (*Zeit. Biol.*, 1900, 40, 535—559).—The observations were made on the salivary glands. Various crystalloids were introduced into the blood and the effect noted. Thus sugar acts only in producing hydræmic plethæra, sodium chloride passes in varying proportions into the secretion, and urea is a mere stimulator of secretory activity. The main idea underlying the work is the same as that in the authors' previous work on lymph formation. They consider they have proved their point concerning the individuality and selective activity of different groups of secreting cells. W. D. H.

Salivary Secretion. By ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1901, 4, 482—499).—The whole theory of secretory nerves is combated, and atropine (which has hitherto been regarded as affording proof of the existence of such nerves) is stated to act directly in the secreting cells, and not on the nerves at all. W. D. H.

Osmotic Pressure of Dog's Submaxillary Saliva. By PIERRE NOLF (*Bull. Acad. Roy. Belg.*, 1900, 960—977).—The osmotic pressure of dog's saliva obtained by excitation of the chorda tympani is variable ($\Delta = 0.195^\circ$ to 0.396°); the saliva secreted spontaneously is more dilute ($\Delta = 0.109^\circ$ to 0.266°). The tension is due almost exclusively to the salts. The tension rises when external pressure is opposed to the salivary flow. W. D. H.

[Value of Alcohol as a Source of Muscular Energy.] By AUGUSTE CHAUVEAU (*Compt. rend.*, 1901, 132, 65—70; 110—114).—The experiments recorded show that alcohol is little, if at all, used as a source of muscular energy. If an isodynamic quantity is substituted for sugar in a diet, the result is unfavourable both as regards the subject of the experiment as a whole and as regards the quantity of work he can do. W. D. H.

Fat Absorption. By IMMANUEL MUNK (*Chem. Centr.*, 1901, i, 52, from *Centr. Physiol.*, 1900, 14, 409—412).—In reference to work of Henriques and Hansen (*Abstr.*, 1900, ii, 668), it is pointed out that if a mixture of fat and paraffin is given to an animal, there is no ground for believing that a uniform emulsion is formed in the intestine. The paper also contains polemical matter in answer to Pflüger (*ibid.*, ii, 667). W. D. H.

Sugar Formation from Fat. By HARTOGH and O. SCHUMM (*Chem. Centr.*, 1901, i, 53; from *Arch. exp. Path. Pharm.*, 1900, 45, 11—45).—In animals in which diabetes had been induced by phloridzin, the relation between the nitrogen and sugar in the urine

indicates that the latter cannot arise from proteid. The conclusion is drawn that the sugar originates from fat. W. D. H

Chemical Composition and Nutritive Value of Different Kinds of Meat. By ADOLF BEYTHIEN (*Zeit. Nahr.-Genussm.*, 1901, 4, 1—9).—Tables giving comparative mechanical and chemical analyses of the various parts of the carcasses of oxen, sheep, and pigs, also including codfish and salt herrings.

The analysis contains no novel details except that the author prefers estimating the water by difference. The proteids were estimated by the Kjeldahl-Gunning method, the nitrogen being multiplied by 6.25. It appears that from an economical standpoint the use of beef (ribs and flank) is preferable to other flesh food. L. DE K.

Metabolism in Horses. By NATHAN ZUNTZ (*Landw. Versuchs-Stat.*, 1901, 55, 117—128).—A reply to Pfeiffer (*Abstr.*, 1900, ii, 554), in which the author maintains that the method employed by himself, in conjunction with Lehmann and Hagemann, is not merely the only satisfactory one for ascertaining the effect of work, including eating, on metabolism, but that it is eminently suited for judging the work of digestion. N. H. J. M.

Asparagine as a Foodstuff. By FRANZ ROSENFELD (*Zeit. Ver. deut. Zuckerind.*, 1900, 1055—1079).—After giving an account of the literature on the feeding of animals with materials of which asparagine forms a part, the author describes his own experiments which were made on a dog. The animal was fed regularly with weighed quantities of various foods, the fæces and urine being collected and examined. The experiments do not lead to any definite conclusions, but seem to confirm the previously observed fact that for carnivorous animals the proteids are better foodstuffs than the amides, in particular than asparagine. T. H. P.

Transformation and Regeneration of Organs. By JACQUES LOEB (*Amer. J. Physiol.*, 1900, 4, 60—68).—In many lower animals (for instance, polyps), parts cut off will regenerate, but change of external conditions will often cause the new growth to be different from the old. This is regarded as due to ionic action, or to the activity of enzymes. W. D. H.

Artificial Parthenogenesis. By JACQUES LOEB (*Amer. J. Physiol.*, 1901, 4, 423—460. Compare *Abstr.*, 1900, ii, 608).—Further experiments are recorded which are confirmatory of the author's views. W. D. H.

[**Parthenogenesis.**] By YVES DELAGE and MARCEL DELAGE (*Compt. rend.*, 1900, 131, 1227—1229).—The importance attributed to magnesium by Loeb in the production of artificial parthenogenesis has led the authors to determine the proportion of this metal in the ash of the male and female organs in animals; they find 8.8 per cent. in the ash in the male, and 7.8 in the female glands. W. D. H.

Effect of Temperature on the Activity of the Upper Cervical Ganglion. By F. C. EVE (*J. Physiol.*, 1900, 26, 119—124).—The upper temperature limit which paralyses the ganglion in cats is 50°. The lower limit varies from 10° to 18°, but recovery occurs on warming. These temperatures are approximately those which are compatible with recovery in human beings. W. D. H.

NOTE.—No reference is made to the work of Marinesco, or of Goldscheider and Flatau, who have shown that the upper temperature limit (about 47°) is that at which chromatolysis of nerve-cells occurs; or to the work of Mott and Halliburton, who have pointed out that this temperature coincides with the heat coagulation temperature of cell-globulin, and have thus furnished a chemical explanation of death from hyperthermia. W. D. H.

Studies on the Liver. I. Absorption in the Liver. By K. BÜRKER (*Pflüger's Archiv*, 1901, 83, 241—352).—The following conclusions are drawn from experiments on rabbits. Heidenhain's theory of interlobular absorption cannot be correct; absorption occurs much more within the liver lobules. The part played by the lymph vessels is well demonstrated by injecting milk into the bile duct; in a short time, the lymphatics become white. The outflow of bile varies in fairly regular periods of 20—30 minutes. Bile secretion sinks much more rapidly in a hungry than in a feeding animal. The normal pressure in the larger ducts is 75—80 mm. of bile, and is not greater than the pressure in the portal vein. In certain pathological conditions, the pressure increases. If the bile duct is entirely closed, the secretory action of the liver diminishes and necrotic changes may occur in the liver. Physiological salt solution, blood, peptone, urea, sodium glycocholate, diluted ox-bile, solution of bilirubin (slightly), and sugar (greatly) are absorbed at one and a half times the pressure of the bile. W. D. H.

Conversion of Creatine into Creatinine by a Soluble Dehydrating Ferment in the Organism. By ERNEST GÉRARD (*Compt. rend.*, 1901, 132, 153—154).—The cold aqueous extract of the cortex of the kidney of the horse, when mixed with chloroform and creatine and heated at 40°, converts a portion of the base into creatinine, negative results being obtained with the previously boiled extract. The amount of creatinine formed is small, but it was identified with certainty by Weyl's reaction and also by separation in the form of phosphotungstate. The dehydrating action is probably due to a soluble ferment and a similar effect was noticed by Abelous and Ribaut, in the synthesis of hippuric acid as brought about by means of the extract of kidneys (*Compt. rend. Soc. Biol.*, 1900, 52, 543). G. T. M.

Presence of Free Aspartic Acid in the Animal Organism. By MARTIN HENZE (*Ber.*, 1901, 34, 348—354).—*Tritonium nodosum* possesses a pair of glands each consisting of two parts; the anterior portion has an alkaline reaction and is non-excreting, whilst the posterior portion, when stimulated, excretes an acid fluid which immediately becomes turbid, and deposits a crystalline compound, identified

as aspartic acid. The fluid, when obtained by electrical stimulus, also gives the reaction of peptones. The aspartic acid is present in the fluid before excretion, for a freshly excised gland placed in boiling water to prevent the action of enzymes yields the characteristic copper salt on treatment with cupric acetate; moreover, the acid may be precipitated in a crystalline form within the substance of the gland itself by soaking the organ in alcohol. Aspartic acid, being soluble in salt water, is in all probability employed by the animal in destroying the calcareous shells of the other shell-fish which form its food. G. T. M.

Camphor Excreted by an Animal (Polyzonium). By O. F. COOK (*Chem. Centr.*, 1901, i, 191; from *Science*, N.S., 1900, 12, 516—521).—The excreta of *Polyzonium rosalbum* have the characteristic odour of camphor. The camphor probably serves as a means of protection. E. W. W.

Quantitative Relationships of Carbohydrates in Diabetic Urine. By HEINRICH ROSIN (*Chem. Centr.*, 1901, i, 227; from *Centr. med. Wiss.*, 1900, 38, 851).—From the quantity of benzoyl esters obtained by Baumann's method, normal urine was calculated to contain 1.5—5.09 grams of carbohydrates, whilst in diabetic urine, after fermentation of the dextrose, 9.17—20.6 grams of carbohydrates still remained. The amount of dextrose does not bear any fixed relationship to that of the carbohydrates determined by means of their benzoyl esters. E. W. W.

Benzoyl Esters and Carbohydrates in Normal and in Diabetic Urine. By VON ALFTHAN (*Chem. Centr.*, 1901, i, 227; from *Centr. med. Wiss.*, 1900, 38, 851—852. Compare preceding abstract).—In the amount of carbohydrates determined by means of the benzoyl esters, animal gum and pentoses are included. Diabetic urines were examined as follows. After estimating the total carbohydrates by Baumann's method, the sugar was fermented and the remaining carbohydrates again converted into benzoyl compounds. The latter were then hydrolysed, and the products treated with alcohol. In this way, the amount of carbohydrates insoluble in alcohol was found to be 6—10 times greater in urines which had not been previously fermented than in those which had. The insoluble portion contained animal gum and glycogen, whilst pentoses and probably isomaltose were present in the portion soluble in alcohol obtained from unfermented urines. E. W. W.

Action of Various Salts on Ciliary and Muscular Movements in Arenicola Larvæ. By RALPH LILLIE (*Amer. J. Physiol.*, 1901, 5, 56—85).—A pure sodium chloride solution destroys ciliary activity, causing liquefaction of the cilia. The injurious effect on muscle in the same animal is less marked. The addition of calcium chloride delays the injurious action on muscle, whilst magnesium chloride is better for this purpose in the case of ciliary movement. Solutions containing no sodium deprive muscle of contractility, but cilia will act well in solutions of other salts, especially magnesium and calcium chlorides in suitable proportions, in the entire absence of sodium. Several other differences are noted with other salts. Such observations weaken a

very general theory that all contractile tissues have a common (? fibrillary) basis of structure.

W. D. H.

Cantharidin and Cantharidin-immunity. By ALEXANDER ELLINGER (*Chem. Centr.*, 1901, i, 54; from *Arch. exp. Path. Pharm.*, 45, 89—109).—Certain animals, like the hedgehog and hen, show great resistance to cantharidin. The present experiments on the hedgehog confirm this. In this animal, doses fatal to other animals have little or no effect, and the substance passes unchanged into the urine. Repeated injection gives rise to chronic nephritis. The resistance of the hedgehog's kidneys to cantharidin is specific, for potassium chromate is as poisonous to these animals as to the rabbit. The hedgehog's skin shows no resistance to the blistering property of cantharidin.

W. D. H.

Action of Chloroform and Ether on the Neurons of Rabbits and Dogs. By HAMILTON WRIGHT (*J. Physiol.*, 1900, 26, 30—41). The bio-physical explanations of narcosis and sleep advanced by Demoor, Lugaro, &c., are combated. The action of the anæsthetics is believed to be bio-chemical. Chloroform is more active than ether. Dogs are more resistant than rabbits, and do not show histological changes in the nerve-cells until anæsthesia is prolonged for 4 hours.

W. D. H.

Physiological Action of Melanoidin and Spongio-melanoidin. By MAX ROSENFELD (*Chem. Centr.*, 1901, i, 54; from *Arch. exp. Path. Pharm.*, 1900, 45, 51—55).—Melanoidic acid, prepared according to Schmiedeberg's method from fibrin by boiling with hydrochloric acid, when injected intravenously produces convulsions and death. The melanin-like substance which contains iodine, and can be prepared from bath-sponge, is not so poisonous. Both substances passed unchanged into the urine.

W. D. H.

Action of Mucus on the Organism. By ALBERT CHARRIN and MOUSSA (*Compt. rend.*, 1901, 132, 164—166).—Mucus collected from the trachea, and dissolved in dilute solution of sodium carbonate, produces, in rabbits, death by causing intravascular coagulation. The agent is believed to originate from the cells contained in the mucus.

W. D. H.

NOTE.—No mention is made of nucleo-proteid, or of the well-known fact that this substance from most animal cells will produce the same effect.

W. D. H.

Physiological Action of Substances from the Thyroid. By E. VON CYON and AD. OSWALD (*Pflüger's Archiv*, 1901, 83, 199—206).—Thyreoglobulin is regarded as the albuminous substance which holds the iodothyryn complex in its molecule. Other constituents of the thyroid which contain iodine have not the physiological characters of iodothyryn.

W. D. H.

Synthesis in the Animal Organism. II. Compounds of the Camphor Group. By HERMANN HILDEBRANDT (*Chem. Centr.*, 1901, i, 53—54; from *Arch. exp. Path. Pharm.*, 1900, 45, 110—129. Compare Abstr., 1900, i, 676).—When sabinol (compare Abstr., 1900, i,

402) is administered to dogs or rabbits, it causes vomiting and stupefaction; the urine becomes laevorotatory, reduces Fehling's solution, and after repeated doses contains *p*-cymene and cumic acid. Since the ester of sabinol is hydrolysed in the organism, it is also probable that when oil of savin itself is used, cumic acid is present in the urine. Thujon from *Oleum thujæ* has a poisonous action similar to that of sabinol; the urine does not, however, contain cumic acid, but *potassium thujonoglycuronate*, $C_{16}H_{28}O_8K$, may be isolated from it. This salt forms white crystals, melts at 240° , and is dextrorotatory, but not so strongly as

thujon itself. After feeding with citral, $Me_2\cdot CH\cdot CH_2\cdot CH_2\cdot \overset{\overset{Me}{|}}{CH}\cdot CHO$,

from lemon-grass oil, or with geraniol, the urine contains a dibasic acid, $Me_2\cdot CH\cdot CH_2\cdot CH_2\cdot C(CO_2H)\cdot CH\cdot CO_2H$, which melts at 187° , is optically inactive, and combines with bromine (4 atoms). When, however,

the stereoisomeric citral, $Me_2\cdot CH\cdot CH_2\cdot CH_2\cdot \overset{\overset{Me}{|}}{CH}\cdot CHO$ is used, only glycur-

onic acid compounds are found in the urine. Cumic acid is not formed either in the case of citral or of geraniol. E. W. W.

Physiological Action of Extracts of Nervous Tissues. By WILLIAM D. HALLIBURTON (*J. Physiol.*, 1901, 26, 229—243).—When injected intravenously, saline extracts of nervous tissues produce a fall of arterial pressure. This is neutralised by atropine. These effects are explicable on the assumption that choline is the active agent present, and this view was confirmed by the separation of choline, as platinichloride, from the solutions. These results show that lecithin, especially in the most active part of the nervous system, namely, the grey matter which yields the most active solutions, is in that continual unstable state of chemical equilibrium called metabolism.

W. D. H.

Veratrine-like Action of Glycerol. By H. WILLOUGHBY LYLE (*Proc. Physiol. Soc.*, 1901, xxvi).—Cleghorn finds that extracts of sympathetic ganglia produce a fall of blood pressure (Abstr., 1899, ii, 569). This Halliburton (see preceding abstract) attributes to choline. Glycerol, however, which was mainly used by Cleghorn to make his extracts, is not physiologically inactive. It produces a fall of arterial pressure which is not abolished by atropine, and it has a veratrine-like action on striped muscle, which was incorrectly attributed by Cleghorn to some substance derived from the ganglia. This action of glycerol on muscle has been previously noted by Langendorff (Du Bois Reymond's *Archiv*, 1891, 480).

W. D. H.

Physiological Relations of Intermittent Albuminuria. By ALBERT CHARRIN (*Compt. rend.*, 1900, 131, 1234—1236).—Two cases of intermittent albuminuria show that the amount of albumin varies with the toxicity, density, and cryoscopic characters of the urine, and with the blood pressure. The explanation of such cases is that they have partly a chemical (disorder of nutrition) and partly a physical (circulatory pressure) origin.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation Experiments with Various Yeasts and Sugars. By PAUL LINDNER (*Chem. Centr.*, 1901, i, 56—57; from *Woch. Brau.*, 17, 713—716).—In these experiments, 21 kinds of sugar and allied compounds were treated with various yeasts of widely different fermenting powers. The mixture of the substance with yeast and water was placed in a hollow object glass, and the air excluded from the cavity by means of a cover-glass. Arabinose, xylose, rhamnose, and the mixture of *l*-sorbose and *d*-galactose were not fermented by any yeast. *d* Glucoheptose only underwent a slight fermentation in one case, and trehalose was not affected by most of the yeasts. Dextrose resisted the action of only three kinds; *d*-mannose and *d*-galactose were fermented by isolated species which also decomposed dextrose, but *l*ævulose was attacked by all those yeasts which fermented dextrose. Inulin was, generally speaking, readily attacked by most of the yeasts. Dextrin (acid-dextrin) was decomposed by several moulds and also by several varieties of yeast including the beer yeast, *Saccharomyces pombe*, *S. octosporus* and *S. mellacei*. Sucrose was fermented by the yeasts of low fermenting power and by the polygonal yeasts, milk sugar by three yeasts from Armenian mazun, Weigmann's yeast, *Sachsia suaveolens*, and possibly by *Monilia variabilis*, and melibiose by some yeasts slightly and by others more strongly. Raffinose did not behave in every case like sucrose; the experiments gave no indication of the presence of the enzyme raffinase. The mixture of real and false tagatose was only moderately attacked by one yeast; false tagatose gave negative results in every case. α -Methylglucoside was fermented by many of the yeasts, but β -methylglucoside by few. According to Fischer's theory, since these compounds are related as object to image, the decomposing agents must be similarly related, hence those kinds of yeasts which ferment both compounds together should contain two different enzymes.

E. W. W.

Arsenic Mould (*Penicillium Brevicaule*). By B. GOSIO (*L'Orosi*, 1900, 23, 361—377).—See this vol., ii, 193.

Presence of a Proteolytic Ferment in Germinated Seeds and its Action. II. By WL. BUTKEWITSCH (*Chem. Centr.*, 1901, i, 190; from *Ber. bot. Ges.*, 1900, 18, 358—364. Compare Abstr., 1900, ii, 744).—The ferment contained in germinated seeds of lupin and other plants may be extracted by glycerol, and is precipitated from the extract by alcohol.

By the action of the ferment on conglutin, leucine, and tyrosine are formed, but asparagine could not be detected, and its absence is in accordance with E. Schulze's theory that it is not a primary product of the decomposition of albumin.

E. W. W.

Digestion in the Ascidia of *Nepenthes*. By GEORGES CLAUTRIAU (*Chem. Centr.*, 1901, i, 57—58; *Mém. Acad. Roy. Belg.*).—The *Nepenthes* contain a zymase, which, in acid solution, has a peptonising action. As in the case of *Drosera*, contact with some object causes an abundant flow of an acid and an enzyme, and in both cases a glutinous material also exudes. After digestion, the ascidia contain a large quantity of liquid, which has frequently an amber colour. This colour is due to a substance which is turned red by alkalis; its origin is unknown; it is not a digestion product allied to tryptophan or a chromogen, for trypsin-like enzymes and amino-acids have not been found in the *Nepenthes*, but it is probably a dye derived from the tannins present in the glands. Experiments in glass vessels show that a peptonising zymase is present in the fluid from the ascidia, but digestion can only be induced at a temperature far higher than that which obtains in the ascidia. Since, too, in the plants themselves the albumin disappears very rapidly, the proteids may possibly be absorbed without previous digestion. *N. melamphora* is capable of digesting albumoses, although these substances are not directly diffusible. As the albumin decomposes it is quickly absorbed. When the ascidia are full of insects, putrefaction sets in, but the plant is not injuriously affected, since it can absorb nitrogen as ammonia or amino-acids. The proteid ammonia disappears, therefore, very quickly in the ascidium fluid, and during digestion the plant requires a supply of nitrogenous food, more particularly as it generally lives as a parasite, and is thus incapable of obtaining nitrogen in the usual way. The plants may possibly also absorb a portion of the mineral substances of the insects.

E. W. W.

Effect of Osmotic Pressure on the Form and Structure of Plants. By J. BEAUVERIE (*Compt. rend.*, 1901, 132, 226—229).—Water culture experiments are described in which *Phaseolus*, *Pisum*, *Lupinus*, *Zea*, and *Triticum* were grown in water alone, in Knop's solution, and in the same liquids with increasing amounts of sodium chloride up to 1.5 per cent. In water, the roots of the *Leguminosæ* bent at an angle of 90° when they came in contact with the liquid, and branched out above or just below the surface. Even with Knop's solution there was a tendency for the branch roots to grow upwards. Addition of sodium chloride to Knop's solution caused this irregularity to disappear; as the strength of the solution was increased, the roots went deeper, except in the case of wheat, whilst the aerial portions of the plants were stunted.

N. H. J. M.

Rôle of the Chlorophyllic Function in the Evolution of Terpenoid Compounds. By EUGÈNE CHARABOT (*Compt. rend.*, 1901, 132, 159—161. Compare *Abstr.*, 1900, i, 241, 303; ii, 101, 361, 362; this vol., i, 38; ii, 34).—Specimens of *Mentha piperita* having green leaves were found to yield an essence containing 9.8 per cent. of ethers, 9.8 per cent. of menthone, and 42.1 per cent. of total menthol; the oil from the red-leaved variety of this plant contained 4.7, 17.1, and 48.3 per cent. of ethers, menthone, and total menthol respectively. Lavender plants deprived of their inflorescences yield an oil containing 39.2 per cent. of ethers, whilst the essence from the complete plant contains only

36.2 per cent. Analyses of the essential oils of plants cultivated under dissimilar hygrometric conditions indicate that dry air favours the formation of ethers.

The transformation of the terpenoid alcohols of plants into their corresponding ethers and terpenes is due to the influence of the chlorophyllic function, and those changes in the environment which strengthen this function are consequently favourable to the genesis of the products of dehydration.
G. T. M.

Production of Proteids in Plants in Absence of Light. By M. IWANOFF (*Landw. Versuchs-Stat.*, 1901, 55, 78—94).—Roots of *Brassica napus* and *Daucus carota*, and potato tubers were kept in darkness for some weeks. The roots and tubers were analysed before and after the formation of leaves.

In two cases, there was a rather slight increase in proteids, but on the whole the results indicate that the formation of proteids goes on in darkness. Even if the increase in proteids as found is assumed to be due to error, the amount of proteids could only remain equal in the very improbable event of the growth having taken place without loss of proteids. A considerable amount of proteids was found in the leaves of *Brassica napus*, and this must have been newly formed proteid unless it had migrated from the roots in the form of albumin or peptone.

A considerable production of proteids can only take place in darkness when the object contains abundance of amides and considerable amounts of readily available carbohydrates, as is the case with bulbs of *Allium cepa* (compare Prianischnikoff, Abstr., 1900, ii, 233).

N. H. J. M.

Reproduction of Proteids from the Products of their Decomposition. By ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1901, 55, 33—44).—Replying to Prianischnikoff (Abstr., 1900, ii, 233), the author states that he has obtained new evidence that asparagine can be produced from other products of the decomposition of proteids (*Ber. deut. bot. Ges.*, 1900, 18, 36).

From the results of experiments in which plants of *Phaseolus vulg.* were analysed after being kept for some days in 1 per cent. glycerol, Prianischnikoff concluded that the slightly increased percentage of proteid nitrogen did not indicate that there had been a regeneration of proteids. It is pointed out that only a small increase, or no increase at all, is no evidence that proteids have not been regenerated; an increase in proteids can only take place when the production in some parts of the plant is in excess of the loss in other parts. In absence of light, the production of proteids can only be considerable when all the other conditions are exceptionally favourable, when proteids are present only in small amount, and when amides and reducing sugar are abundant.

The author considers that Prianischnikoff's observations are in no way opposed to his own results, and only criticises his conclusions.

N. H. J. M.

The Manna of Olives. By TRABUT (*Compt. rend.*, 1901, 132, 225—226).—The olive trees of the village of Mansourah in the Pro-

vince of Bibans are subject to a disease of bacterial origin communicated by the inoculation of the cortex by certain insects, probably locusts. The bacteria develop in the cambium and provoke the complete decomposition of the cortex and the exudation of a sugary product resembling the manna of the ash. This substance, called by the natives "Assal zitoun," the manna of olives, contains 52 per cent. of mannitol, 7·8 per cent. of reducible sugar, and 21·5 per cent. of other organic matter, a portion of which is precipitable by alcohol. The wood which is laid bare by the decomposition of the cortex undergoes a very marked change and becomes veined and blackened.

G. T. M.

Presence of Sucrose in Panama Wood. By G. MEILLÈRE (*Bull. Soc. Chim.*, 1901, [iii], 25, 141—142).—The carbohydrate contained in the wood of *Quillaia smegmadernos*, hitherto considered the same as Meyer's lactosin, is now shown by its physical and chemical properties to be identical with sucrose.

N. L.

Chemical Composition of the Coffee of Grande Comore. By GABRIEL BERTRAND (*Compt. rend.*, 1901, 132, 162—164).—The berries from *Coffea Humblotiana* found on the island of Grande Comore differ from those of *C. Arabica* or *C. Liberia* in containing no caffeine; experiments made on 1 kilo. of the material failed to reveal any trace of this alkaloid. The difference is not due to the soil or the climate in which the plant is cultivated, for *C. Arabica* grown under precisely similar conditions still yields the normal amount of caffeine.

G. T. M.

Autumnal Return of Substance in Hops. By C. FRUWIRTH and W. ZIELSTORFF (*Landw. Versuchs-Stat.*, 1901, 55, 9—18).—The results of the authors' experiments indicate that a portion of the nitrogen, potash, and phosphoric acid of the leaves and stems of hops return to the roots in the autumn.

N. H. J. M.

Ivy as a Calcareous Plant. By W. VON KLENZE (*Chem. Centr.*, 1901, i, 225; from *Zeit. landw. Vers.-Wes. Oester.*, 3, 629—630).—The air-dried wood of ivy yielded 2·57 per cent. of ash containing 31·09 of lime and 4·52 per cent. of magnesia. Ivy is thus undoubtedly a calcareous plant. It is not suitable for fodder, and is almost free from parasites.

E. W. W.

Nitrogenous Constituents of the Seeds and Seedlings of *Lupinus Albus*. By NICOLAI J. WASSILIEFF (*Landw. Versuchs-Stat.*, 1901, 55, 45—77).—White lupin seeds contain more total and proteid nitrogen than blue, but less than yellow lupins (compare E. Schulze, *Landw. Jahrb.*, 1878, 7, and Merlis, *Abstr.*, 1898, ii, 133).

Seedlings of white lupins 7 days old contained in the cotyledons tyrosine, leucine, arginine, and histidine, whilst it is probable that phenylalanine, aminovaleric acid, and leucine are present in the axils.

The leaves of seedlings 2 weeks old did not contain much amino-acid; leucine and perhaps aminovaleric acid were found, but not tyrosine. The leaves also contained asparagine and vernine and, probably, xanthine.

The following numbers show the amounts of nitrogen (per cent. of total N) in different forms in the seeds and seedlings (7 and 14 days old) of *Lupinus albus*.

| Nitrogen in | Seeds. | Seedlings. | |
|-----------------------------------|--------|------------|----------|
| | | 7 days. | 14 days. |
| Proteids | 89.69 | 42.47 | 43.47 |
| Phosphotungstic acid precipitate. | 6.90 | 10.56 | 7.63 |
| Asparagine..... | — | 32.15 | 39.79 |
| Other amides | 3.41 | 14.82 | 9.11 |

From these results, it might be supposed that vegetation in presence of light and the production of carbohydrates have only a slight effect on the reproduction of proteids from amides. The decomposition of the reserve proteids was, however, not completed in 7 days; moreover, the plants acquired considerable amounts of nitrogen from outside and contained a good deal of nitrogenous matter for the production of proteids, much of which material remained after 14 days.

The fact that at the end of the second week much of the nitrogen was in the form of asparagine accords with E. Schulze's assumption that asparagine is produced from other products of the decomposition of proteids. This explains how it is that the asparagine does not decrease in quantity notwithstanding its utilisation for proteid formation. Whilst the leaves contained 22.66 per cent. of proteids and 6.75 per cent. of asparagine, the stems contained 9.56 per cent. of proteids and 21.12 per cent. of asparagine.

N. H. J. M.

Production of Brewing Barley with Low Percentage of Nitrogen on Light Soils. By THEODOR RÉMY (*Bied. Centr.*, 1900, 27, 809—811; from *Bl. Gersten-, Hopfen-, u. Kartoffelbau*, 1900, 51).—When, as in Brandenburg, sandy soils are periodically liable to suffer from insufficiency of water, the whole of the assimilable nitrogen, intended for large crops, is available; the result is a crop rich in nitrogen. In such cases, the seed should be sown early and the soil should be deeply worked before the winter and harrowed in the spring. The most suitable amount of nitrogen for a particular soil and climate can only be determined experimentally. As regards the form of nitrogen to be applied, nitrate will give satisfactory results if the climate and other conditions are favourable during the later stages of growth, but not otherwise. Ammonium salts, and especially organic nitrogen, are safer manures, as they act more slowly and do not promote the early growth to the same extent as nitrate.

To obtain barley poor in nitrogen, the yield must be increased as much as possible without increased application of nitrogen; the land must be well prepared and suitable plants selected.

N. H. J. M.

Composition of Grasses from Different Meadows. By ADOLPH EMMERLING, C. WEBER, FR. BACHÉ, and H. HILBERT (*Bied. Centr.*, 1900, 29, 804—807. Compare *ibid.*, 1894, 23, 517).—It was previously shown that the chemical composition of good varieties of grass is not essentially different from that of inferior varieties, and that Wittmack's botanical method of analysis is uncertain for valuing hay, but is of greater importance in the case of pasture.

In the experiments now described, the grasses were grown together on three different soils. The results showed that there is no relation between the amounts of nutritive matter and the variety of the grass, or between the average composition of the superior grasses and that of the inferior grasses, which could be utilised in valuing the grasses according to the botanical composition. The value of hay can therefore only be ascertained by chemical analysis.

N. H. J. M.

Effect of Different Amounts of Inoculating Material on the Production of Nodules and the Yield of Leguminosæ. By FRIEDRICH NOBBE and LORENZ HILTNER (*Landw. Versuchs-Stat.*, 1901, 55, 141—148).—The results of nitrogen experiments with peas and *Vicia villosa* showed that the amount of inoculating material has no influence within the limits of 1:10,000. Nitragin may be diluted a hundred times without any diminution in effect. Owing, however, to the various losses to which bacteria are exposed in the soil, it would not be advisable in practice to employ the amount of nitragin hitherto applied to $\frac{1}{4}$ hectare for larger areas.

N. H. J. M.

Utilisation of Gorse. By ANTOINE CHARLES GIRARD (*Ann. Agron.*, 1901, 27, 5—44).—Attention is called to the importance of gorse for feeding, and as litter and green manure. Gorse grows on soils poor in mineral matter, and obtains its large amount of nitrogen by fixation. It is estimated that a crop of 20,000 kilos. may be obtained per hectare, and that this is equivalent to 8000 kilos. of hay.

The average composition of the samples of gorse analysed is as follows: Water, 52.67; nitrogenous matter, 4.55; fat, 0.90; non-nitrogenous extract, 25.99; cellulose, 14.32, and ash, 1.57 per cent. The amounts of sugars, pentosans, and pectic substances are: 1—1.8; 8—10, and 1.1—2.2 per cent. respectively. The ash contains K_2O , 27.13; CaO , 11.71; MgO , 4.28; Fe , 1.66; P_2O_5 , 6.71, and SO_3 , 4.68 per cent.

The results of feeding experiments with a horse show that the following percentage amounts of the different constituents were digested: Ash, 40.4; fat, 21.6; nitrogenous matter, 56.0; crude cellulose, 42.8; sugars, 100; saccharifiable substances, 54.7; total non-nitrogenous extract, 54.6. Less satisfactory results were obtained with a sheep.

N. H. J. M.

Influence of Feeding on [the Composition of] Butter. By H. WEIGMANN and OTTO HENZOLD (*Chem. Centr.*, 1901, i, 132—133; from *Milch-Zeit.*, 29, 737—738, 756—758).—The change from pasture to stall feeding resulted in a slight decrease in the volatile fatty acids (about 19—17.5); a further change, in which wheat bran was substituted for a portion of the mixed hay food, caused a great depression (to 13.83), which, however, only lasted for 2 days; this depression was followed by a permanent increase (20—22). The great decrease in volatile fatty acids is attributed to the change rather than to the nature of the food.

Further experiments showed that a change of food only affects the amount of volatile fatty acids when the foods are very dissimilar. Straw, linseed, and poppy-seed cakes are unfavourable to the produc-

tion of volatile fatty acids. At the beginning of the period of lactation, crushed rye, wheat bran, cotton seed cake, and green fodder increase the amounts of volatile fatty acids. N. H. J. M.

Changes in the Fat During the Ripening of Cheese. By KARL WINDISCH (*Chem. Centr.*, 1901, i, 128—130; from *Arbb. K. Ges.-A.*, 17, 1—160).—During the ripening of cheese, large amounts of free acids are produced by the decomposition of the fat. At the same time, the Reichert-Miessl and refractometer numbers are gradually reduced as are also, to a less extent, the saponification numbers. The acids are mainly non-volatile higher acids, volatile fatty acids being formed only in relatively small amounts. The decrease of volatile fatty acids during ripening and storing is of importance in distinguishing genuine from margarine cheeses. A margarine-Edam cheese did not produce an appreciable amount of volatile fatty acids in three years, whilst in margarine-Romadur cheese there was a slight production of volatile acids in ten months.

The changes which cheese undergoes are similar to the changes in butter which becomes rancid, although the changes in cheese are much greater. In rancid butter and lard, however, the iodine number decreases, whilst during the ripening of cheese it first gradually decreases and then increases.

The glycerol liberated during the ripening of cheese gradually disappears, being probably destroyed by microbes.

The chief cause of the decomposition of cheese fat is the action of microbes, some of which probably produce enzymes; these break up the glycerides, and in this way produce food suitable for the microbes. The decomposition of the glycerides is also partly due to the action of ammonia which is produced, along with soluble proteids and amides, by the action of microbes on paracasein.

Henzold's process for separating cheese fat (*Abstr.*, 1896, ii, 680), was found to be unsuitable. The hydrochloric acid process (*Arbb. K. Ges.-A.*, 14, 554, and *Chem. Centr.*, 1898, ii, 932), in which all the fatty acids, including those in combination with ammonia, are obtained, was employed. N. H. J. M.

Examination of the Bog Earth of Bad-Sülze, and Göldenitz, with a Comparative Table of Certain Bog Earths. By PAUL HOFFMANN (*Zeit. anal. Chem.*, 1901, 40, 22—33. Compare *Abstr.*, 1899, 798, 799).—The examination of the soil of these two bogs was undertaken to ascertain their suitability for the preparation of medicinal baths, for which purpose the presence of ferrous sulphate and sulphuric acid in an aqueous extract is generally considered requisite. From the very small amount of these substances in some bog earths of notable therapeutic value, the author is, however, inclined to doubt whether the beneficial action is entirely to be attributed to them. Two samples of the Sülze bog earth were analysed, both in the fresh condition and after 6 months' weathering. Only in one of the weathered samples was a trace (0.12 per cent.) of iron soluble in water found. Since the dry earth contained 6.99 and 4.63 per cent. of iron, chiefly in the form of disulphide, it is probable that with

longer weathering some of it would become soluble. The dry, un-weathered samples contained in 100 parts :

| Soluble in water. | | | | Soluble in acid (HCl). | | | | |
|--------------------|--------------------|-------------------|------|------------------------|-------------------|---------------------------------|------|----------------------------------|
| Mineral substance. | Organic substance. | SO ₃ . | CaO. | Mineral substance. | SO ₃ . | P ₂ O ₅ . | CaO. | Fe ₂ O ₃ . |
| 1. 8.17 | 1.12 | 0.69 | 0.16 | 20.44 | 1.09 | 0.18 | 4.47 | 0.68 |
| 2. 2.38 | 0.44 | 0.35 | 0.14 | 6.48 | 0.38 | 0.10 | 0.03 | 0.97 |
| Total sulphur. | | Humic acid. | | Humin. | | Cellulose. | | |
| 1. | 9.93 | 3.62 | | 10.41 | | 7.1 | | |
| 2. | 6.42 | 7.98 | | 3.28 | | 7.34 | | |

A small quantity of free sulphur was present ; nitrites were found, also formic and tannic acids, but no acetic acid.

The dry substance of the Göldenitz earth is almost wholly (97.3 per cent.) organic, with only 0.146 per cent. of iron. It is therefore of use solely as a cheap fuel.

M. J. S.

Employment of Pepsin Solution for Investigating Fæces and Stable Manure. By THEODOR PFEIFFER and OSCAR LEMMER-MANN (*Landw. Versuchs-Stat.*, 1900, 55, 129—140. Compare Abstr., 1886, 1053, and Kühn, *ibid.*, 1894, ii, 389).—The authors consider that Pfeiffer's method is preferable to that proposed by Bülow (Abstr., 1900, ii, 459), but that Bülow's results, indicating that the substance may be dried at 55—60°, are of great importance. The following method has recently been employed by the authors.

The finely cut and well mixed manure (100 grams) is digested for 48 hours at 38—40° with 500 c.c. of Wedemeyer's pepsin solution and hydrochloric acid (Abstr., 1899, ii, 460). The solution is neutralised as exactly as possible, evaporated to dryness, weighed, and finely ground ; 5 grams are used for estimating the indigestible nitrogen in the usual manner.

The opinion has been expressed (this vol., ii, 37) that the varying effect of stable manure is due to different degrees of decomposition. Samples of fresh manure containing the same amount of dry matter (35.8 grams) were made equally moist by adding water and 20 c.c. of soil extract, and kept for three months at 38°. The samples were then examined by the method just described, when it was found that the "digestibility" had not, as was expected, increased, but diminished in different degrees. Pot experiments were made with fresh manure and with manure which had been kept ; the results showed a good deal of similarity with those of the digestive experiments, and although there were divergences which cannot be explained, the new method is considered promising.

N. H. J. M.

Analytical Chemistry.

Arrangements for Electrolytic Analysis. By HUGH MARSHALL (*J. Soc. Chem. Ind.*, 1900, 19, 992—994).—A convenient and compact apparatus and equipment of the usual type for electrolytic analysis, which cannot be well understood without the accompanying illustrations. L. DE K.

The Electrolysis of Copper Sulphate as a Basis for Acidimetry. By CHARLES A. KOHN (*J. Soc. Chem. Ind.*, 1900, 19, 962—963).—The author prepares a sulphuric acid the actual strength of which is accurately known by submitting a solution of twice recrystallised copper sulphate to the usual electrolysis. The metal is weighed and the corresponding acid calculated. By means of the dilute acid so obtained, the strength of alkaline solutions may be accurately determined. L. DE K.

The Preparation of an Exact Standard Acid. By C. LONGUET HIGGINS (*J. Soc. Chem. Ind.*, 1900, 19, 958—962).—The processes which have been proposed from time to time for the preparation of an exact standard acid are reviewed, and the conclusions drawn that the only really trustworthy method is that based on the absorption of hydrogen chloride by water as proposed by Moody (*Trans.*, 1898, 73, 658).

The author had independently conceived the same idea, his apparatus being, however, somewhat different. Hydrochloric acid is allowed to run from a separating funnel into strong sulphuric acid contained in a generating flask, the gas evolved passes first through two wash-bottles containing sulphuric acid and then into a specially constructed absorption bulb, fitted with a capillary delivery tube provided with a two-way tap, and containing a known weight of water. When sufficient gas is supposed to have been absorbed, the bulb is disconnected and reweighed. An acid of known composition is thus obtained.

L. DE K.

Ferrisalicyclic Acid as an Acidimetric Indicator. By J. E. GEROCK (*Chem. Centr.*, 1900, ii, 1294; from *Ann. Chim. anal. appl.*, 5, 421).—Ferrisalicyclic acid is a very serviceable indicator in some special cases, but cannot replace the ordinary indicators for general purposes.

M. J. S.

Separation and Identification of Acids. By RICHARD ABEGG and W. HERTZ (*Zeit. anorg. Chem.*, 1900, 25, 405—406).—In reply to Fresenius (*Abstr.*, 1900, ii, 754), the authors agree that hydrocyanic and arsenious acids are not precipitated by calcium chloride. The first would be precipitated in the zinc group along with ferrocyanide and ferricyanide; in presence of these, it is recognisable by the smell of hydrocyanic acid, produced by warming with dilute sulphuric acid. The second must be tested for by hydrogen sulphide. The complete precipitation of tartaric acid by calcium chloride is not necessary, since

the small quantity remaining in solution does not interfere with subsequent tests. Boric acid is recognised by the green alcohol flame in the portion of the calcium precipitate which is soluble in acetic acid.

T. E.

Detection of Chlorates and Bromates by the Use of Strychnine. By FAGES (*Chem. Centr.*, 1901, i, 202—203; from *Ann. Chim. anal. appl.* 1900, 5, 441).—Chlorates and bromates produce a red coloration in a solution of strychnine nitrate. 0.81 gram of strychnine is dissolved in 24 c.c. of nitric acid of sp. gr. 1.334 and 1—2 drops of the chlorate solution are added to 1 c.c. of the reagent. The reagent must always be present in excess. With traces of chlorate, the coloration requires 16—20 minutes to develop. Hypochlorites, chlorine, bromine, hydrochloric acid, nitrites, chlorides (if in large excess), and especially ferric chloride, hinder the reaction; iodates and perchlorates neither produce nor prevent the reaction. The red substance is not removed by carbon disulphide, ether, chloroform, or benzene. The reagent will not keep for 24 hours. M. J. S.

Estimation of Fluorine in Zinc Blendes. By FRIEDRICH BULLNHEIMER (*Zeit. angew. Chem.*, 1901, 101—104).—Satisfactory results were not obtained when using Bein's process (heating with sulphuric acid and quartz powder, passing the vapours into water, and collecting the precipitated silica), as only about one-third of the fluorine present was found. Good results were, however, obtained by means of a modification of the process devised by Fresenius.

The apparatus consists of an Erlenmeyer flask of 300—400 c.c. capacity provided with a treble-perforated indiarubber cork. Through one of the holes passes a thermometer, through the others, the inlet and exit tubes. The latter is connected with a U-tube filled with glass-wool which is in turn connected with a Winkler worm tube, which may be surrounded by cold water, and is fitted to the absorption apparatus, consisting of a Dreschmidt wash-bottle containing 80 c.c. of solution of potassium chloride. For passing a current of air, Fresenius's directions should be followed.

If the apparatus is found to be air-tight, 2.5 grams of the finely powdered sample intimately mixed with 3—5 grams of powdered quartz are put into the flask, 20 grams of chromic acid dissolved in 100 c.c. of strong sulphuric acid are added and the cork is at once inserted. Purified air is now passed through the apparatus, and the flask is slowly heated on an iron or aluminium plate to about 80°; when action sets in, great heat is developed, and the source of heat may be temporarily removed; afterwards the temperature may be raised to 150—160°. After heating for three hours, all the silicon fluoride is expelled and absorbed in the wash-bottle. To the contents of this is now added an equal volume of alcohol, and after some time the liquid is rapidly titrated with *N*/10 sodium hydroxide, using phenolphthalein as indicator. One c.c. of *N*/10 alkali corresponds with 0.005685 gram of fluorine. L. DE K.

Detection of Added Sulphuric Acid in Wine. By F. CARPENTIERI (*Chem. Centr.*, 1900, ii, 1216; from *Staz. sperim. agrar. ital.*, 33, 307—340).—The new process is based on the determination of the

relation between ash and sulphuric acid. Pure wines investigated by the author showed the following relation. When the wine contains from 0.0—1 per thousand of sulphates ($\frac{1}{2}$ potassium sulphate) the relation is as 8.3 : 2.93, for 1.1—2 as 3.29 : 2.00, for 2.1—3 as 2.23 : 1.55, and for more than 3 as 1.42 : 1.18.

The proportion is diminished if the wine has been mixed with sulphuric acid either during or after the fermentation. If the wine has been neutralised previously to adding the acid, the test becomes useless. If the neutralisation has been effected by potash, the comparative soluble and insoluble alkalinity may give a clue. L. DE K.

Amount of Selenium in Sulphuric Acid. By N. A. ORLOFF (*Chem. Zeit.*, 1901, 25, 66).—The author does not approve of the codeine test for selenium as proposed by Schlagdenhauffen and Pagel (*Abstr.*, 1900, ii, 342), but has obtained satisfactory results by applying the sulphurous acid test.

Five parts of the sample of sulphuric acid to be tested are mixed with 10 parts of water and 10 parts of solution of sulphurous acid; the selenium is then precipitated slowly in the cold, and more rapidly on warming, and may be collected and weighed. The author did not meet with any selenium in the pure German or Russian acid, but a Russian crude acid contained 0.024 per cent. of selenium. Acid of French origin was not at the author's disposal. The sulphurous acid test serves to detect as little as 0.003 per cent.; for still smaller quantities, the codeine test is quite untrustworthy. L. DE K.

Detection of Ammonia by Mercuric Chloride. By ANNIBALE FERRARO (*Chem. Centr.*, 1901, i, 203; from *Boll. Chim. Farm.*, 1900, 39, 797).—The precipitate produced by mercuric chloride in natural waters free from ammonia is readily soluble in a small excess of cold acetic acid, but if ammonia is present the precipitate dissolves only very slowly and requires much acid. Nessler's reagent should, however, be employed as a confirmatory test. M. J. S.

Analysis of Nitric and Mixed Acids by Du Pont's Modification of Lunge's Nitrometer. By J. R. PITMAN (*J. Soc. Chem. Ind.*, 1900, 19, 982—984).—The author prefers using the apparatus devised by Du Pont instead of the Lunge nitrometer, as it is possible to make a duplicate analysis of nitric acid or a mixed acid within half an hour. As the quantity operated on may be five or six times as large as when using Lunge's nitrometer, the results are consequently more accurate.

The apparatus should be standardised by means of pure potassium nitrate and a particular specimen of sulphuric acid, the same volume of which is used in the testing of the samples. No readings of temperature or pressure are then required. L. DE K.

Estimation of Phosphoric Acid in Basic Slags. By A. N. PAPEŽ (*Chem. Centr.*, 1900, ii, 1213—1214; from *Zeit. landw. Vers. Wes. Oest.*, 3, 695—713).—The author states that the conventional methods for the estimation of the citrate solubility, the citric acid solubility, the solubility in 5 per cent. formic acid, and the total phosphoric acid all give satisfactory results. As regards the Austrian nitric acid

method for estimating the phosphoric acid, the author recommends boiling the slag with nitric acid of sp. gr. 1.25. L. DE K.

Detection of Mineral Phosphates in Basic Slags. By NORBERT VON LORENZ (*Chem. Centr.*, 1900, ii, 1213; from *Zeit. Landw. Vers. Wes. Oest.*, 3, 684—686).—Mineral phosphates almost invariably contain fluorides, therefore when fluorine is present in a basic slag, an admixture of mineral phosphate is probable. The method formerly recommended by the author (Abstr., 1888, 1340) is not suitable for basic slag on account of its being interfered with by the presence of sulphides. To detect fluorine in basic slags, the convex side of the watch glass is covered with a piece of filter-paper moistened with 5 per cent. aqueous soda, the paper is then washed with a little water and the liquid is tested for fluorine by adding acetic acid and calcium acetate. A turbidity or precipitate either before or after boiling shows the presence of fluorine. Superphosphates, bone meal, and animal charcoal may be similarly tested for mineral phosphates. L. DE K.

Chemical Examination of Soil. By GEORG BERJU (*Landw. Versuchs-Stat.*, 1901, 55, 19—31).—In extracting soils with 1 per cent. citric acid solution, agitation for 6 hours one day and for 2 hours the next day in a Wagner's rotatory apparatus is sufficient as regards calcium and potassium, and, in the case of most soils, for phosphoric acid also. Continued agitation for 8 hours does not have the same effect.

In the case of humous loamy soil, the above treatment seems to be insufficient, and the soils should be agitated with the solvent for at least 7 days, unless it is considered that the phosphoric acid dissolved by the more prolonged treatment is less assimilable.

The fact that the potassium of sandy loams and loams is sparingly soluble in 1 per cent. citric acid is perhaps due to the absorptive power of these soils for assimilable potash. The result of experiments by Knop's method showed that the absorptive power for ammonia and potash is very slightly reduced by 1 per cent. citric acid. The relation of the solvent to the soil was, however, only 2 : 1 in these experiments, whilst in extracting the soils 10 parts of citric acid solution were used with 1 part of soil. N. H. J. M.

Arsenic Mould (*Penicillium Brevicaule*). By B. GOSIO (*L'Orosi*, 1900, 23, 361—377).—This organism is capable of killing by ingestion, as was shown in the case of some rabbits kept in a chamber in which the mould was being grown.

The use of *Penicillium brevicaulis* for detecting the presence of arsenic has been applied to natural waters, the intestines in cases of suspected poisoning, coloured materials, chemical products, physiological secretions and minerals, in all cases with satisfactory results.

The gas evolved by this organism in the presence of an arsenic compound (shown by Biginelli to be diethylarsine, this vol., i, 20) may be detected otherwise than by its odour, by passing it into a solution of 8 to 12 parts of mercuric chloride and 20 parts of hydrochloric acid in 80 parts of water, when a crystalline mass is gradually formed at the point where the gas bubbles through the liquid. T. H. P.

Biological Test for Arsenic. By BRUNA GALLI-VALERIO and CASIMIR STRZYZOWSKI (*Chem. Centr.*, 1901, i, 63; from *Pharm. Post.*, 33, 637—639, 649—651. Compare *Abstr.*, 1900, ii, 299).—By the action of *Penicillium brevicaulis* on a millionth of a gram of arsenious oxide, mixed with about 5 grams of bread crumbs, the characteristic arsenical odour was developed in 3 days, and in 2 days more it still remained distinctly perceptible, but had become less marked. In the case of a patient who had taken 44 milligrams of arsenic in 8 days, arsenic could be detected by this test in the tears, mucous membrane of the nose, saliva, and in the ash of the urine and faeces, but not directly in the hair, nails, perspiration, or urine. The composition of the gas liberated by the mould is unknown, but it probably consists of arsines. Small quantities of arsenic are completely volatilised, and the residue is absolutely free from arsenic. E. W. W.

Separation of Arsenic. By MARTIN ROHMER (*Ber.*, 1901, 34, 33—38).—On distilling a solution containing an arsenate to which a small quantity of hydrobromic acid has been added in a stream of hydrogen chloride and sulphur dioxide, the whole of the arsenic is volatilised as chloride, and after absorption in water, the arsenious acid can be estimated either volumetrically, by means of standard iodine, or gravimetrically, by precipitation as arsenious sulphide; the addition of hydrobromic acid accelerates the reduction of the arsenic acid, which otherwise takes place very slowly. If 170 c.c. of solution is distilled until its volume is 40 c.c., a single distillation, occupying about 45 minutes, usually suffices to separate 0.15 gram of arsenic. The sulphur dioxide in the distillate is removed by diluting and boiling for 20 minutes in a reflux apparatus, a stream of carbon dioxide being continually passed through the solution.

If antimony is present, it remains in the distilling flask, and can be estimated by precipitation as sulphide, after boiling to remove sulphur dioxide; the antimony sulphide thus obtained contains varying amounts of sulphur, which cannot be removed by carbon disulphide, but is eliminated by heating for 2 hours at 225—230° in an atmosphere of carbon dioxide. If tin is present as well as antimony, the latter has to be estimated volumetrically. The author is still investigating this case.

Analyses are given showing the degree of accuracy of the method, which indicate that the presence of other metals is not deleterious.

W. A. D.

Analysis of Italian Crude Boric Acid. By E. ZSCHIMMER (*Chem. Zeit.*, 1900, 25, 44—45, 67—68).—The author, as the result of many experiments, has come to the conclusion that for the assay of crude boric acid the titration process is the best and the following scheme is recommended. 1. One gram of the air-dried sample is dissolved in 300 c.c. of pure glycerol with addition of water, and titrated with standard barium hydroxide, with phenolphthalein as indicator; when a pink coloration is produced, more glycerol is added, and should the colour disappear, the titration is continued. 2. One gram of the sample is dissolved in water and in the filtrate any sulphuric acid is estimated. 3. A few mixtures of boric acid and ammonium sulphate of known composition are made and titrated as

before, so as to know once for all how many c.c. of barium hydroxide solution correspond with 1 gram of sulphur trioxide present as ammonium sulphate. 4. A blank experiment should be made to determine any accidental acidity in the glycerol. 5. From the number of c.c. of barium hydroxide solution used for 1 gram of the sample are deducted the number of c.c. corresponding with the sulphur trioxide and those required by the glycerol. The balance is then calculated to boric acid. Very concordant results were obtained.

L. DE K.

Adulteration of Roasted Coffee by means of Addition of Water and Borax. By E. BERTARELLI (*Zeit. Nahr.-Genussm.*, 1900, 10, 681—683).—The author calls attention to the fact that some dealers soak the roasted coffee berries in a boiling 5 per cent. solution of borax, the berries then reabsorb the greater part of the moisture lost during the roasting.

The amount of borax introduced is, however, not large enough to perceptibly increase the ash. If, therefore, a sample of roasted coffee berries shows an excess of moisture, borax may be suspected and should be tested for in the usual way.

L. DE K.

Behaviour of Borax on Distillation with Methyl Alcohol. By EDUARD POLENSKE (*Chem. Centr.*, 1901, i, 15; from *Arbb. Kais. Ges.-A.*, 17, 564—568).—When borax is distilled with methyl alcohol, 57—59 per cent. of the boric acid passes into the distillate, of which the first portions contain by far the greatest part. By adding ether to the residue, sodium metaborate, $\text{NaBO}_3 \cdot 5\text{MeOH}$, is obtained. The borax is not directly decomposed into boric acid and sodium oxide by distilling with the alcohol, but first forms sodium metaborate and boric acid. The metaborate is then attacked, and the decomposition continues until the composition of the residue corresponds with $\text{Na}_{10}\text{B}_8\text{O}_{17}$. This residue is not homogeneous, but probably contains sodium metaborate and sodium oxide, the excess of the latter preventing further decomposition. Hönig and Spitz's volumetric method is thus correctly based on the existence of sodium metaborate. When C. Fresenius and Popp's method is used for the examination of sausage which contains borax alone, the complete volatilisation of the boric acid is due to the decomposition of the borax in the original material; in this case, the sausage has a faintly acid reaction.

E. W. W.

Apparatus for the Auto regulation of Combustion in Organic Analysis. By E. A. GANIKE (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 819—825).—A description, with figures, is given of an electrical contrivance, by means of which the height of the flame of the two burners directly under the boat containing the substance to be burnt in a combustion tube is regulated according to the rate at which the products of combustion bubble through the potash bulbs.

T. H. P.

Estimation of Potassium by Perchloric Acid in Commercial Analyses. By CARLO MONTANARI (*Chem. Centr.*, 1901, i, 203—204; from *Staz. sperim. agrar. ital.*, 1900, 33, 454).—A solution of perchloric acid is prepared by shaking 100 grams of sodium perchlorate

with 150 grams of pure concentrated hydrochloric acid, filtering through glass wool, and expelling the hydrochloric acid from the filtrate by evaporation. Half a gram of substance, freed from ammonia and sulphates, is dissolved in 15—20 c.c. of water and mixed while warm with 1 c.c. of the reagent. The mixture is evaporated until volatile acids are expelled, and after cooling is stirred with 20 c.c. of 95 per cent. alcohol to which 2 vols. per cent. of perchloric acid solution are added. After some hours, the precipitate is collected on a Gooch filter, washed with 60—70 c.c. of the same acid-alcohol and then once or twice with alcohol alone. After drying at 120—130°, the precipitate is weighed, removed from the filter with hot water, and the tare taken. Owing to a slight solubility of the precipitate, the results are about 0.258 per cent. (of K_2O) lower than those obtained with platinic chloride, and this correction may be applied. M. J. S.

Estimation of Potash in Soil. By A. RÜMLER (*Landw. Versuchs-Stat.*, 1901, 55, 149).—The soil is extracted on a filter with definite amounts of lime water or a solution of potassium [? calcium] chloride. It is supposed that the potassium liberated by these solvents is that available for plants. Pot experiments are being made to ascertain whether this is the case. N. H. J. M.

Estimation of Lead in Galena. By M. WILLENZ (*Chem. Centr.*, 1900, ii, 1292; from *Ann. Chim. anal. appl.*, 5, 401).—The presence of calcium does not prevent the estimation of lead as sulphate, if the following process is adopted. One gram of the ore is dissolved in nitric acid, the solution evaporated with 5 to 6 c.c. of concentrated sulphuric acid, then treated with 50 c.c. of water and heated for 15—20 minutes on the water-bath, cooled, decanted through a filter, and the precipitate washed once with a 1 per cent. sulphuric acid and thrice with cold water. It is then dissolved in 25 c.c. of a feebly ammoniacal 33 per cent. solution of ammonium acetate, the solution filtered, washed with a 5 per cent. solution of ammonium acetate, and the lead precipitated by adding 5—6 c.c. of sulphuric acid. If some calcium sulphate should also be thrown down at this stage, the liquid is decanted, 1 to 2 c.c. of sulphuric acid and 250 c.c. of water are added to the precipitate, and the whole heated in the water-bath for an hour with frequent stirring. The lead sulphate is then treated in the usual way. In presence of antimony, some tartrate is added when dissolving. Copper is thrown down from the first filtrate by sodium thiosulphate, at the boiling temperature, after adding 10 c.c. more of sulphuric acid. M. J. S.

Volumetric Estimation of Thallium. By HUGH MARSHALL (*J. Soc. Chem. Ind.*, 1900, 19, 994—995).—About 0.2 gram of the thallic compound is dissolved in water, a crystal of potassium bromide is added, and then 25 c.c. of a standard solution of sodium bromate containing 2.467 grams of the salt per litre. After quickly adding a sufficiency of dilute hydrochloric acid, the mixture is distilled, and the liberated bromine estimated as usual. The loss in bromine represents the thallium. The author titrates the bromine

in the presence of potassium iodide with a solution of 5 grams of sodium thiosulphate in a litre of water; 1 c.c. of this represents 0.002 gram of thallium. The solution does not keep well, and should therefore be checked against 25 c.c. of the bromate solution.

The apparatus consists of a glass-stoppered, round-bottomed flask, with a side tube connected with a vertically placed spiral condensing tube, surrounded by a glass condenser, which dips into a bottle-shaped receiver containing a solution of potassium iodide. The hollow stopper of this bottle carries a side exit tube containing glass beads, also moistened with solution of potassium iodide, so as to ensure complete absorption of the bromine.

L. DE K.

Analysis of Commercial Copper. By P. TRUCHOT (*Chem. Centr.*, 1901, i, 204—205; from *Ann. Chim. anal. appl.*, 1900, 5, 444).—Five to ten grams of the copper are dissolved in 25—50 c.c. of nitric acid, with addition, finally, of bromine or hydrogen peroxide. The filtered solution is electrolysed with a current of 0.8—1.2 volts, and after 15—18 hours the precipitated lead is collected, dissolved in hydrochloric acid and evaporated with sulphuric acid, taken up with water, the precipitate collected on the same filter, washed well with weak sulphuric acid, dissolved in ammonium acetate, and the filtrate electrolysed after adding nitric acid, when pure lead is obtained. For estimating the cobalt, nickel, and manganese, the first filtrate is evaporated with sulphuric acid; arsenic, antimony, and tin are removed by hydrogen sulphide, iron by precipitation, twice repeated, with ammonium carbonate, manganese thrown down as phosphate from a strongly ammoniacal solution, and nickel and cobalt precipitated by electrolysis.

M. J. S.

Estimation of Copper in Pyrites. By OLE N. HEIDENREICH (*Zeit. anal. Chem.*, 1901, 40, 15—17).—In solutions containing much iron, copper cannot be directly estimated by electrolytic precipitation. A preliminary precipitation with aluminium is much more convenient than the use of zinc or hydrogen sulphide. The solution must be evaporated with hydrochloric acid until free from nitric acid. It is then acidified with hydrochloric acid and treated with aluminium foil at a gentle heat. The washed mixture of precipitated copper and excess of aluminium is then dissolved in dilute nitric acid, and the solution electrolysed in the usual manner, after addition of a little sulphuric acid. Small amounts of cobalt, nickel, zinc, and lead are without influence on the results.

M. J. S.

Separation of Metals by means of Acetylene. By HENRIK G. SÖDERBAUM (*Bihang Svenska Vetensk.-Akad. Handl.*, 1900, 25, ii, No. 5, pp. 1—25. Compare *Abstr.*, 1897, ii, 348, and 1898, ii, 191).—The use of acetylene for the estimation of copper in mixtures of its salts with those of other metals has been extended to the following separations.

Copper from zinc.—The conditions given for the separation of copper from cadmium (*loc. cit.*) yield good results, the zinc being determined in the filtrate either as oxide or sulphide, or volumetrically by means of potassium ferrocyanide solution.

Copper from nickel.—In this case, the copper acetylide must be

washed, first with cold or tepid water, and afterwards, when the greater part of the ammonia has been removed from the precipitate, with boiling water; if the filtrate is turbid, or the filter paper coloured reddish-brown in places, the washing has been improperly carried out.

Copper from cobalt.—The same precautions as regards washing must be taken as with nickel; the cobalt is determined electrolytically as metal.

Each of the above separations has been tested for a number of different ratios between the quantities of the two metals present in the mixtures, the results being very satisfactory. T. H. P.

Detection of Alum in Wines. By FRANCESCO LOPRESTI (*Chem. Centr.*, 1900, ii, 1216; from *Staz. sperim. agrar. ital.*, 33, 373—377).—Fifty c.c. of the sample are evaporated to about one-third, and decolorised with animal charcoal. The filtrate is carefully neutralised with sodium or potassium hydroxide, and diluted to 50 c.c. A few drops of freshly prepared tincture of logwood are added, which cause a violet or blue coloration if alum is present; in its absence, the liquid is merely orange-yellow. L. DE K.

Solubility of some Metallic Oxides in Sodium and Ammonium Salicylate. By JULES WOLFF (*Chem. Centr.*, 1901, i, 207; from *Ann. Chim. anal. appl.*, 1900, 5, 445).—Cupric hydroxide dissolves in cold concentrated solution of salicylic acid, and with excess of sodium hydroxide a blue solution resembling Fehling's solution is produced. The copper sodium salicylate, $(\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2)_2\text{Cu}$ can be obtained in moss-green crystals containing water of crystallisation which they lose in dry air.

Ferric and aluminium hydroxides are also soluble in ammonium salicylate, and from this solution hydrogen sulphide precipitates the iron completely, leaving aluminium in solution. By evaporating the filtrate and heating at 200° , pure alumina is left. M. J. S.

Proximate Analysis of Clays. By W. JACKSON and E. M. RICH (*J. Soc. Chem. Ind.*, 1900, 19, 1087—1088).—It is shown that the conventional proximate analysis of clays, by means of hot sulphuric acid gives altogether untrustworthy results, particularly in the case of plastic clays, as any felspar present is largely attacked by both the acid and the subsequent alkaline treatment. L. DE K.

Testing of Weldon-deposit. By KONRAD W. JURISCH (*Zeit. angew. Chem.*, 1901, 3). Reply by GEORG LUNGE (*ibid.*, 60).—Jurisch states that Hurter originated the process of testing Weldon-deposit by means of a normal solution of oxalic acid.

In reply, Lunge states that Weldon deserves the credit of having worked out the process. L. DE K.

Estimation of Manganese and Chromium in Tungsten Alloys. By FRED IBBOTSON and HARRY BREARLEY (*Chem. News*, 1900, 82, 209—210).—Manganese is estimated in tungsten powder and alloys by treating 1 gram with 10 c.c. of hydrofluoric acid and 4 c.c. of nitric acid, adding, when action slackens, 2 or 3 c.c. of sulphuric acid, then oxidising, and titrating in the usual way. As a rule,

these alloys and powders contain less than half a per cent. of manganese; in the case of alloys, sometimes met with, containing 10 per cent. of manganese, not more than 0.1 gram should be used.

In the estimation of chromium in alloys of iron, chromium, tungsten, and manganese, the alloy is digested with a mixture of sulphuric and hydrofluoric acids, treated with a few grams of solid permanganate, then diluted and boiled with excess of permanganate until solution is complete. Or it may be dissolved in nitro-hydrofluoric acid, boiled with sulphuric acid until sulphur trioxide is evolved, and then be diluted for further treatment.

D. A. L.

Analysis of Ferro-silicons and Silico-spiegel. By FRED IBBOTSON and HARRY BREARLEY (*Chem. News*, 1900, 82, 269—270).—Ferro-silicon and silico-spiegel not being amenable to treatment with copper solutions, the *total carbon* is estimated by combustion in a current of oxygen; the *graphite* by treating 2—3 grams with 70—100 c.c. of nitric acid of sp. gr. 1.2, exciting, and gently maintaining the action by adding a few drops of hydrofluoric acid; the graphite is collected and washed successively with water, boiling sodium hydroxide, dilute hydrochloric acid, and again with water, and ultimately burnt in oxygen. *Silicon* is estimated by boiling 2 grams of the finely powdered alloy, until decomposition is complete, with 50 c.c. of concentrated hydrochloric acid and 10—20 c.c. of nitric acid, adding twice the volume of water, filtering at once, washing with dilute hydrochloric acid, igniting, and weighing; a correction of 0.1 per cent. for soluble silica being made. *Manganese* is estimated by dissolving 1 gram in 30 c.c. of nitric acid of sp. gr. 1.2 and 1 or 2 c.c. of hydrofluoric acid, cooling, adding 10 c.c. of water, then about 2 grams of sodium bismuthate, filtering, adding standard hydrogen peroxide, and titrating with *N*/10 permanganate (Reddrop and Ramage, *Trans.*, 1895, 57, 268). With silico-spiegels, the solution of the alloy is made up to 100 c.c., and 25 c.c. are treated with nitric acid, &c. The *phosphorus* is estimated by treating 2 grams of the finely-powdered alloy with 45 c.c. of nitric acid of sp. gr. 1.2 and 25—30 drops of hydrofluoric acid, the latter treatment being once repeated when action first subsides; when decomposition is complete, permanganate is added until manganese dioxide is precipitated, and then ferrous sulphate to clear the solution, which is filtered, treated with 6 to 7 c.c. of ammonia, precipitated with ammonium molybdate, and the lead molybdate weighed (compare *Abstr.*, 1900, ii, 757); any phosphorus in the hydrofluoric acid must be allowed for.

D. A. L.

Estimation of Tungsten in Steel and Steel-making Alloys. By FRED IBBOTSON and HARRY BREARLEY (*Chem. News*, 1900, 82, 224—225).—Five grams of the steel or alloy are digested below the boiling point in 100 c.c. of strong hydrochloric acid with nitric acid in quantity only slightly above that required to keep the iron in the ferric state; the solution is boiled until the tungsten trioxide commences to separate, it is then diluted with at least twice its volume of water, and boiled. The precipitate of tungsten trioxide, silica, and a little iron is further treated. When ferro-tungstens are treated in this way, the tungsten remaining in solution must be recovered by

evaporation and included. With nickel-tungstens, hydrofluoric and nitric acids are required, the latter being ultimately expelled by boiling with sulphuric acid; the solution is then diluted and filtered, and the tungsten trioxide weighed whilst the nickel is estimated cyanometrically. If silica and molybdenum are also to be determined in the nickel-tungstens, hydrochloric and not hydrofluoric acid is used. Tungsten-molybdenum steels are treated in quantities of from 2 to 3 grams with hydrochloric and nitric acids, evaporated to pastiness, boiled with dilute hydrochloric acid, the tungsten trioxide weighed, and the molybdenum estimated as lead molybdate (Abstr., 1900, ii, 766).

In addition to the ordinary constituents in tungsten powders, a substance in the form of bronze to brown cubes or tetrahedra of a specific gravity of 7.3 has been isolated, by sifting through a 60 mesh sieve, boiling some portion with sodium hydroxide, washing, drying, digesting with nitrohydrofluoric acid, and washing and boiling the residue with sodium hydroxide.

D. A. L.

Schöffel's Process for Estimating Tungsten in Steel. By ERNEST BAGLEY and HARRY BREARLEY (*Chem. News*, 1900, 82, 270—271).—In working by Schöffel's method (Abstr., 1880, 288), the residue is liable to contain a variety of substances which are largely eliminated by using the following modification. Five grams of the sample are digested at the boiling point, and occasionally shaken with 50 grams of crystals of cuprammonium chloride, 100 c.c. of water, and 50 c.c. of strong hydrochloric acid; a little while after the precipitated copper has dissolved, the solution is filtered and the residue washed with dilute hydrochloric acid, ignited, silica volatilised by treatment with hydrofluoric acid, the residue fused with sodium carbonate, dissolved in water, and the ferric oxide ignited, &c. The filtrate, if yellow, is acidified with sulphuric acid, treated with ferrous sulphate, titrated with permanganate, and calculated into chromic oxide; this, together with the ferric oxide, is deducted in order to obtain the percentage of tungsten. With less than 1 per cent. of tungsten, only 10 per cent. of hydrochloric acid should be used in the cuprammonium solution, otherwise the results obtained may be low. Molybdenum, if present, may or may not pass into solution; part of the silicon also is dissolved; silicon cannot therefore be estimated by the loss on treatment with hydrofluoric acid.

D. A. L.

Analysis of Uranium and Vanadium Ores. By OLIVER P. FRITCHE (*Chem. News*, 1900, 82, 258).—The method is particularly adapted to the analysis of carnotite. Half a gram of the finely powdered ore is moistened with water, digested at a 'slow boiling temperature' for an hour with 10 c.c. of nitric acid, diluted with 10 c.c. of water, and neutralised with a saturated solution of sodium carbonate, of which 5 c.c. in excess is then added, along with 20 c.c. of a 20 per cent. solution of sodium hydroxide; the whole is boiled slowly for half an hour and allowed to settle. The precipitate containing the iron and uranium is collected, washed with a solution of sodium hydroxide, and dissolved in 20 c.c. of hot (1 : 1) nitric acid; the solution is treated with 40 c.c. of water, then with ammonia, until a permanent precipi-

tate begins to form, finally with 40 c.c. of a fresh saturated solution of ammonium carbonate, and heated to boiling for a few minutes; it is then filtered and washed with a 2 per cent. solution of ammonium carbonate. The filtrate is treated with 20 c.c. of sulphuric acid (1 : 1), boiled until dense fumes are evolved, cooled, diluted to 100 c.c., and boiled with strips of aluminium until the colour becomes sea-green, when the uranium is titrated with permanganate. The iron precipitate is dissolved in hydrochloric acid, boiled with sulphuric acid until dense fumes are evolved, reduced with aluminium, and titrated. For vanadium, half a gram of ore is moistened with water, boiled with 10 c.c. of nitric acid and 10 c.c. of sulphuric acid until the dense fumes appear, reduced with aluminium and titrated; the number of c.c. required less those obtained for the iron and uranium gives the quantity of vanadium.

D. A. L.

New Method for the Volumetric Estimation of Bismuth. By GUSTAV FRERICHs (*Chem. Centr.*, 1901, i, 277; from *Apoth. Zeit.*, 15, 859).—In order to estimate the amount of bismuth in surgical dressings, &c., the sulphide obtained by precipitating with hydrogen sulphide from an acid solution is treated with an excess of *N*/10 silver nitrate solution (1 c.c. = 0.00693 Bi) and 10 c.c. of dilute nitric acid, the volume made up to 100 c.c., the mixture well shaken and 50 c.c. of the filtrate titrated by Volhard's method.

Almost all the metallic sulphides react quantitatively with silver nitrate in a similar manner, forming silver sulphide and the nitrate of the metal.

E. W. W.

Estimation of Oxidisable Substances in Water. By ERNST RUPPIN (*Zeit. Nahr.-Genussm.*, 1900, 10, 676—681).—The author has made a number of experiments to ascertain the influence exercised by chlorides in the estimation of oxidisable organic matters in waters by means of potassium permanganate and has tabulated the results. The experiments were made by adding 9 c.c. of solution of permanganate (0.313 gram of potassium permanganate per litre) to the boiling solution and boiling for 10 minutes; the undecomposed permanganate was then titrated. The liquid was made either acid or alkaline and contained a varying amount of sodium chloride.

From the first series of experiments made with an acid solution, it appears that so long as the amount of chlorine does not exceed 0.200 gram per litre it has no perceptible influence on the titration, but when that amount is exceeded, it rapidly makes its influence felt, so that when it reaches 1.6 grams it accounts for 1.01 c.c. of permanganate, whilst 10 grams destroy 7.15 c.c.

Experiments in which a solution of tartaric acid was used (0.010 gram per litre) with varying amounts of sodium chloride gave similar results, although the action was less marked. As may be expected, the addition of sodium chloride does not affect the titration in an alkaline solution.

Further experiments were made to determine the influence of manganous sulphate, 1 c.c. of a solution of manganous sulphate (200 grams per litre) was added to the water, and also to solutions containing 0.003—0.015 gram of tartaric acid per litre, and it was found that this

was sufficient to prevent the interfering action of chlorine, even if this is present to the extent of 4 grams per litre.

A remarkable result was obtained with water to which a few drops of meat-peptone had been added, but which was free from sodium chloride. It was oxidised in acid solution, in alkaline solution, and in an acid solution with addition of manganous sulphate. The results were respectively 8.23, 22.30, and 11.24 c.c. of permanganate.

L. DE K.

Analysis of Acetylene. By ARNOLD ROSSEL and E. LANDRISET (*Zeit. angew. Chem.*, 1901, 77—82).—A generating flask of 5—6 litres capacity, provided with a safety funnel and gas-delivery tube, is filled with water and calcium carbide is added until the water is saturated with acetylene. After temporarily closing the delivery tube, about 20 grams of the sample of calcium carbide are added, the funnel is inserted, and the gas after passing through a calcium chloride tube is collected over mercury in a Hempel burette. After absorbing the acetylene as usual by means of sulphuric acid, the residual gas is tested for oxygen, hydrogen, methane, and nitrogen by the well-known Hempel methods. Ammonia is always present, more particularly if much magnesium carbide is present. It is a curious fact that when the carbide is thrown into an excess of water no hydrogen sulphide is evolved, whilst by allowing water to drop on to the lumps, the greater part of the sulphur present is evolved as hydrogen sulphide or other thio-compounds. A new apparatus is described for the estimation of the sulphur and phosphorus in calcium carbide.

L. DE K.

Action of Denigès' Acetone Reagent on Terpenes. By CARL GLÜCKSMANN (*Chem. Centr.*, 1901, i, 135; from *Zeit. Oesterr. Apoth.-V.*, 38, 1085).—Denigès' reagent, a solution of 5 grams of mercuric oxide in a hot mixture of 20 c.c. of concentrated sulphuric acid and 100 c.c. of water, is not a specific reagent for ketones or aldehydes, since it gives white precipitates when shaken with oil of turpentine and the majority of the ethereal oils.

The precipitate seems to contain a mercurous compound, and it is suggested that mercuric sulphate might prove a convenient mild oxidising reagent.

M. J. S.

Estimation of Cyanides and Cyanates. By J. W. MELLOR (*Zeit. anal. Chem.*, 1901, 40, 17—21).—Commercial potassium cyanide may be analysed by the following methods. A solution of 20 grams of the substance in 100 c.c. of water is mixed with calcium nitrate to precipitate carbonates, and the filtrate is made up to 200 c.c. The cyanogen is estimated in 10 c.c. by Denigès' modification of Liebig's method (*Abstr.*, 1896, ii, 385). For the cyanate, 10 c.c. of the solution are mixed with an excess of concentrated silver nitrate solution and the precipitate is washed with ice-cold water. It is then treated with p c.c. of N nitric acid, warmed to 50°, and filtered. The acid in the filtrate is titrated with N sodium hydroxide, n c.c. being required. The percentage of potassium cyanate is then $4.05(p - n)$.

M. J. S.

Wine Analysis. By FRIEDRICH BOLM (*Zeit. Nahr.-Genussm.*, 1900, 10, 667—676).—*Specific gravity and estimation of alcohol.*—As a 50 gram specific gravity bottle is rarely absolutely correct, it is necessary to ascertain its exact capacity; the weight of the wine or of its distillate is then divided by the weight of the water. To save the correction, the author simply deducts 50 grams from the weight of the bottle filled with water at 15.5°, calls the difference the weight of the empty bottle, and then uses it in wine analysis as if it were perfectly correct. Provided the bottle holds an amount of water not greatly differing from 50 grams, the results will be correct to the fourth decimal. *Estimation of the extract.*—In order to prevent the extract from absorbing moisture, the platinum dish is cooled in a desiccator containing asbestos or pumice moistened with sulphuric acid and then introduced into a suitable weighing glass. *Estimation of the mineral constituents.*—As the ash is hygroscopic, the crucible should be inserted in a weighing glass. In the author's opinion it is unnecessary to moisten with ammonium carbonate and to again dry; treatment of the moist ash with free carbon dioxide should be resorted to. *The normal solutions.*—*N/3* soda is recommended for estimating the acidity &c., and a table and suitable formulæ are given to facilitate the calculations. *Estimation of the sugar.*—Reference is made to a former paper by the author (*ibid.*, 1899, 2, 689). It is stated that it is not strictly necessary to remove tannins before applying the copper test. Attention is again called to the great difficulty of obtaining cuprous oxide free from contaminating organic matters. L. DE K.

Examination of Glycerol. By CALIXTE FERRIER (*Chem. Centr.*, 1901, i, 136; from *Mon. Sci.*, [iv] 14, ii, 808).—Owing to the presence of fusible salts, it is impossible to completely incinerate the carbonaceous residue of commercial glycerol without serious loss of mineral matter by volatilisation.

The charred residue should therefore be crushed and exhausted with water, the solution being withdrawn by a capillary pipette which does not admit the solid particles. The carbon then burns easily, the solution is added to the ash, evaporated, and gently ignited.

M. J. S.

Analysis of Surgical Dressings. By GUSTAV FRERICHS (*Chem. Centr.*, 1901, i, 209—210; from *Apoth.-Zeit.*, 15, 832, 839, 849).—In commercial analyses of surgical dressings, it is usual to report the amount of the antiseptic constituent per 100 parts of the unimpregnated fabric. It is therefore necessary to dry and weigh the fibre after exhaustion with appropriate solvents, and allow for 5 per cent. of moisture in the original material.

Carbolic Acid Dressings.—Koppeschaar's method, as modified by Beckurts, is used; 10 grams of the dressing are extracted with 500 c.c. of cold dilute sodium hydroxide; 50 or 25 c.c. are mixed in a stoppered bottle with 50 c.c. each of potassium bromide (5.94 grams per litre) and potassium bromate (1.667 grams per litre), and 5 c.c. of concentrated sulphuric acid. After 15 minutes, a gram of potassium iodide is added, and the iodine titrated by *N/10* thiosulphate.

Salicylic Acid is estimated in a similar manner (compare Freyer, Abstr., 1897, ii, 608).

Iodoform.—Lehmann's method is used (Abstr., 1900, ii, 372, 776; this vol., ii, 42).

Mercuric Chloride.—For undyed dressings, Beckurts' process may be used; 20 grams of the dressing and 0.5 gram of sodium chloride are treated with 500 c.c. of water. To 250 c.c. of the solution, diluted to 500 c.c., 0.2 gram of ferrous sulphate and an excess of sodium hydroxide are added; the mixture is then acidified with sulphuric acid, an excess of *N*/100 iodine is added, and the excess titrated by thiosulphate. If the fabric is dyed, the mercury must be precipitated as sulphide, the sulphide be treated with *N*/100 iodine, sulphur removed by carbon disulphide, and the iodine titrated.

Boric Acid.—Beckurts' and Danert's method (*Apoth.-Zeit.*, 12, 159; *Chem. Centr.*, 1897, i, 771). *Bismuth*.—See this vol., ii, 201.

Preparations containing iodine are treated in a nickel capsule with sodium hydroxide and alcohol, the mixture dried at 150° and charred. It is then treated with water and nitric acid, and the iodide in an aliquot portion titrated by Volhard's process. Aristol and europen should be first mixed with 4–6 parts of starch.

Preparations containing silver are incinerated and the silver titrated by Volhard's thiocyanate method. M. J. S.

Estimation of Milk Sugar by Polarisation and Reduction. By ANTON SCHEIBE (*Zeit. anal. Chem.*, 1901, 40, 1–14).—The difference between the results of the optical and reduction methods, when applied to the estimation of milk sugar in milk, which by some observers has been attributed to the presence of a second optically active constituent, disappears completely if due regard is paid to the following considerations, and a process based on them is adopted. The volume of the precipitate produced when freeing the milk from casein must not be neglected. This precaution is more necessary for the optical method than for the reduction method, in consequence of the much greater dilution employed in the latter. The calcium in the milk must be removed, since its presence diminishes the amount of copper reduced by milk sugar. The use of lead acetate for precipitating the proteids must be abandoned, since the optical rotation of milk sugar is influenced by that salt. The volume of the precipitate can be ascertained by adding to the milk a known amount of milk sugar and observing its influence on the optical rotation; calcium may be removed by sodium fluoride, and the lead acetate replaced by a solution of mercuric iodide. The two processes are then conducted as follows. *Gravimetric estimation*: 25 c.c. of milk diluted with 400 c.c. of water are mixed with 10 c.c. of copper sulphate solution (69.28 grams per litre), then with 3.5–4 c.c. of *N* sodium hydroxide and 20 c.c. of a cold saturated solution of sodium fluoride. After half an hour, the whole is made up to 500 c.c.; 100 c.c. of the filtrate are mixed with 50 c.c. of Fehling's solution, boiled for 6 minutes, and the cuprous oxide collected, reduced with hydrogen, and weighed. Soxhlet's table (*Zeit. anal. Chem.*, 20, 436) gives the corresponding amount of milk sugar. *Polarimetric estimation*: 75 c.c. of milk are mixed with 7.5 c.c.

of 20 per cent. sulphuric acid and 7.5 c.c. of mercuric iodide solution (made by dissolving 40 grams of potassium iodide in 200 c.c. of water, shaking with 55 grams of mercuric chloride, making up to 500 c.c., and filtering). The mixture is made up to 100 c.c. and the filtrate polarised. In a second quantity of 75 c.c. of milk, 10 grams of milk sugar ($=M^1$ grams as estimated by polarisation, after mixing with sulphuric acid and mercuric iodide exactly as in the experiment with the milk) are dissolved by warming; after cooling, 0.5 c.c. of strong ammonia is added to destroy mutarotation, and, 10 minutes later, sulphuric acid and mercuric iodide are added as before, and the filtrate polarised. Subtracting the rotation due to the milk alone, the difference (M^2) gives the uncorrected amount of the milk sugar added. The volume (V) of the precipitate is then $100M^2 - 100M^1/M^2$, and the true amount of milk sugar in the milk is obtained by multiplying the apparent amount by $1 - 0.01V$, which for whole milk has the average value 0.94, and for skimmed milk 0.97, but for very rich milk, cream, and colostrum must be specially determined. M. J. S.

Estimation of Sugar by Fehling's Solution. By F. UTZ (*Chem. Centr.*, 1901, i, 277; from *Pharm. Zeit.*, 1900, 45, 998—999).—De Haen's method is recommended, but the cuprous oxide after filtering, washing, and calcining is dissolved in nitric acid and titrated. E. W. W.

Estimation of Cellulose, &c., in Plants, &c. By WILHELM HOFFMEISTER (*Landw. Versuchs-Stat.*, 1901, 55, 115—116).—A reply to Kleiber (*Abstr.*, 1900, ii, 630; compare Hoffmeister, *ibid.*, 1898, ii, 148 and 544). N. H. J. M.

A Reaction of Apiole. By ARMAND JORISSEN (*Chem. Centr.*, 1901, i, 135; from *J. Pharm. Liège*, 7, Oct., 1900).—A dilute alcoholic solution of apiole when treated with chlorine until turbidity is produced, and then with a few drops of ammonia, acquires a transient, brick-red colour. M. J. S.

Volumetric Estimation of Aldehydes. By MAXIMILIAN RIPPER (*Monatsh.*, 1900, 21, 1079—1085).—Twenty-five c.c. of 0.5 per cent. aqueous solution of the aldehyde are mixed with 50 c.c. of standard potassium hydrogen sulphite solution (12 grams per litre) and left for 0.25 hour, the amount of sodium hydrogen sulphite uncombined with the aldehyde is then titrated by the aid of $N/10$ iodine solution. It is not advisable to use stronger solutions of the aldehyde or sulphite than those stated. The method has given good results with formaldehyde, acetaldehyde, benzaldehyde, and vanillin. If the iodine solution contains a considerable amount of potassium iodide in solution, namely, 3 times the weight of the iodine, it may be kept for several months without altering.

A little alcohol may be added to facilitate the solution of the aldehyde, but must never reach 5 per cent. J. J. S.

A New and Sensitive Reaction for the Detection of Formaldehyde and of Lactose in Milk. By E. RIEGLER (*Chem. Centr.*, 1901, i, 206; from *Pharm. Centr. Halle*, 1900, 40, 769).—Formaldehyde and other aldehydes yield a rose-red coloration with phenylhydrazine hydrochloride and sodium hydroxide. About 2 c.c. of milk, 2 c.c. of water, and 0.1 gram of solid phenylhydrazine hydrochloride are placed in a test-tube and shaken until the latter has dissolved, whereon 10 c.c. of 10 per cent. sodium hydroxide solution are added, and the mixture again shaken for half a minute. Normal milk gives no coloration, but milk to which 2 drops of formalin per 100 c.c. have been added acquires a rich rose-red colour in 2—3 minutes. If the same process is repeated with the addition of a little sodium acetate and the mixture is then boiled before adding the soda, the red colour indicates the presence of lactose. M. J. S.

Estimation of Vanillin in the presence of Piperonaldehyde. By JOS. HANUŠ (*Zeit. Nahr.-Genussm.*, 1900, 10, 657—667).—A measured quantity of the solution representing about 0.02—0.15 gram of vanillin is introduced into a 150 c.c. Erlenmeyer flask, 10 c.c. of a 10 per cent. hydrochloric acid solution of platinic chloride are added, and the whole diluted to 50—100 c.c. The flask is heated in a water oven at 70—80° for 1 hour, and then allowed to cool for another hour. The condensation product is collected on asbestos contained in a Gooch crucible, washed until all hydrogen chloride is removed, dried for 3 hours at 100—105°, and weighed. When the amount of vanillin does not exceed 0.06 gram, the quantity represented by the precipitate is calculated by means of the equation $x = y + 15.7/0.97$, but if over 0.06 the formula $x = y + 38.25/1.04$ is employed, in which x equals the vanillin and y the weight of the precipitate.

Piperonaldehyde is not precipitated by platinic chloride, and the process is, therefore, a very suitable one for the estimation of vanillin in the presence of moderate quantities of it. The platinic chloride may be readily recovered from the filtrate and used again.

L. DE K.

The Sensitiveness and Trustworthiness of Certain Methods of Detecting Citric and Tartaric Acids and of One of these in presence of the Other. By GIULIO PARIS (*Chem. Centr.*, 1901, i, 205—206; from *Staz. sperim. agrar. ital.*, 1900, 33, 486).—Athenstädt's method (*Arch. Pharm.*, 1884, 22, 230) gives trustworthy results if freshly filtered saturated lime-water is used and access of atmospheric carbon dioxide prevented. Even 0.007 gram of tartaric acid in 1 gram of citric acid gives a distinct turbidity and the same amount produces a feeble blue coloration by Crismer's method (*Abstr.*, 1892, 546). Pusch's test (*Abstr.*, 1885, 445) is disturbed by the presence of tannic acid or of sugar. Salzer's test (*Abstr.*, 1888, 996) employed in the cold shows about the same limit of sensitiveness as that of Pusch. Mohler's method as modified by Denigès (*Abstr.*, 1896, ii, 80) gives a distinct coloration with 7 per mille of tartaric acid. The best tests are those of Denigès and Mann (*Abstr.*, 1885, 843). M. J. S.

Detection of Cinnamic Acid in presence of Benzoic Acid. By ARMAND JORISSEN (*Chem. Centr.*, 1901, i, 136; from *J. Pharm. Liège*, 7, 185).—Under the influence of light, cinnamic acid is oxidised by uranyl salts to benzaldehyde, which can be recognised by its odour. One gram of benzoic acid is boiled with 10 c.c. of water, the solution cooled, treated with 4 c.c. of a 5 per cent. solution of uranyl acetate, and the mixture exposed to direct sunlight. One per cent. of cinnamic acid can be detected. M. J. S.

Source of Error in Testing Wine for Salicylic Acid. By HENRI PELLET (*Chem. Centr.*, 1900, ii, 1293—1294; from *Ann. Chim. anal. appl.*, 5, 418).—It has been shown by Ferreira da Silva that certain wines free from salicylic acid give up both to ether and to light petroleum a substance which gives the reactions of that acid. The substance is, however, insoluble in a mixture of equal volumes of ether and petroleum, which ought therefore always to be used for the extraction. M. J. S.

Oleum Cacao. By P. WELMANS (*Chem. Centr.*, 1901, i, 194; from *Pharm. Zeit.*, 1900, 45, 959—961).—In reference to the data given by the new German pharmacopœia, the author points out that pure oleum cacao, obtained by pressing the roasted seeds deprived of their pods, generally melts at 34—35°, and in exceptional cases at 33—36°, whilst that obtained by extracting with ether or light petroleum melts at 30—34°, and the fats extracted from pods, &c., have even lower melting points. The fat should be introduced into the melting point tube in a solid form, and not previously melted. The iodine number of pressed fats is usually 34—36, the extracted fats only showing the wider limits 34—38. Determinations of the acid number and the saponification number are also useful in detecting rancidity and impurities.

The iodine number of pure cod liver oil is sometimes as high as 170. E. W. W.

Halphen's Reaction for Cotton Seed Oil. By EDUARD WRANPELMEYER (*Zeit. Nahr.-Genussm.*, 1901, 4, 25—26).—The author does not approve of Soltsien's modification of the Halphen test (*Abstr.*, 1899, ii, 823), in which the amyl alcohol is dispensed with. The substitution of hot water for brine and the use of a condensing tube are, however, recommended. The author now operates as follows. A thick-walled test-tube 2.5 cm. wide and about 15 cm. long, and having a 10 c.c. mark, is filled to the mark with the oil to be tested, and an equal volume of amyl alcohol and 2 c.c. of a 1 per cent. solution of sulphur in carbon disulphide are added. The tube is then closed with a cork through which passes a glass tube 1.5 m. long and $\frac{3}{4}$ cm. wide, and the tube is inserted in the boiling water-bath for $\frac{1}{4}$ hour, when in the presence of even 5 per cent. of cotton seed oil, the characteristic red colour will make its appearance. L. DE K.

Zeiss' Butyro-refractometer. By JOHN WHITE (*J. Soc. Chem. Ind.*, 1900, 19, 1089—1090).—A table is given showing the scale divisions observed in the Zeiss butyro-refractometer for butter, lard,

margarine, olive oil, rape oil, refined cotton seed oil, sesamé oil, castor oil, raw linseed oil, sperm oil, cod liver oil, and mineral lubricating oil at 25°, 40°, and 45°.

To calculate the scale divisions at any observed temperature up or down to any other temperature, a correction of 0.55 scale division should be made. The scale divisions or degrees may be calculated to the actual refractive index; a refractive index of 1.4220 corresponds with 0° and 1.4895 with 100°.

L. DE K.

Examination of Butter and Fats. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1901, [iii], 25, 142—144).—In the ordinary Reichert-Meissl process, the distillate containing the fatty acids is filtered before titration, and the Reichert number thus has reference only to the acids which are both volatile and soluble in water. If, however, the unfiltered distillate is mixed with half its volume of alcohol, the acids insoluble in water are dissolved, and titration then gives the total volatile acids, both soluble and insoluble. The ratio of the soluble volatile acids to the total volatile acids is found to be 0.90 for butter fat and 0.32 for coco fat, whilst intermediate figures are obtained in the case of margarine and lard.

N. L.

Estimation of Fat in Fæces. By H. LÜHRIG (*Chem. Centr.*, 1901, i, 137—138; from *Pharm. Centr. Halle*, 41, 721. Compare Abstr., 1900, ii, 223; and this vol., ii, 78).—A contradiction is given to Oefele's statement that the author has regarded the total ethereal extractive matter as fat. The lecithin was estimated by extracting with alcohol and determining the phosphoric acid in the ash of the alcoholic solution; from this the lecithin was then calculated by multiplying by 7.27. Assuming this to be present as distearyllecithin, the amount of free fatty acid produced by saponification was obtained. Subtracting this from the total amount of insoluble fatty acids, the remainder gave the pure fats. Another method is to saponify the ethereal extractive matter by alcoholic potash and remove the portion insoluble in alcohol and hot water. The filtrate, freed from alcohol, is then shaken with light petroleum, the residue from the petroleum solution again saponified, and shaken once more with petroleum. The petroleum solution is washed with water to remove soap, and evaporated. The fatty acids are then precipitated from the soap solutions. The fatty acids in the ethereal extractive matter vary from 45 to 81 per cent., the lecithin from 23 to 34, and the non-saponifiable constituents soluble in petroleum from 0.8 to 42 per cent.

M. J. S.

Assay of Bees-Wax. By GEORG BUCHNER (*Chem. Zeit.*, 1901, 25, 21—22, 37—39).—Some waxes show abnormal acidity, ether, and saponification numbers, but do not give any reaction for stearic acid, glycerides, resins, paraffins, &c. No wax should therefore be condemned merely because the constants are abnormal, but in such a case, and even when they are normal, the sample should be tested for these admixtures.

The author tests for stearic acid in the usual way by boiling with alcohol and diluting the cold filtrate with water; or instead of water,

an alcoholic solution of lead acetate or calcium chloride may be used, which will detect the presence of as little as 0.2 per cent. of stearic acid. Glycerides, if present in large amounts, may be detected by the odour of acraldehyde, obtained on fusing the sample with potassium hydrogen sulphate; if small quantities are looked for, the sample is saponified with alcoholic potassium hydroxide, the alcohol is expelled, and the residue extracted with water; the solution is then evaporated, and the residue tested for glycerol as before. For the detection of the other adulterants, the author refers to a previous paper (*Abstr.*, 1896, ii, 456) and also to the processes devised by Weinwurm and by Storch, and finally to Werder's method (this vol., ii, 139).

Attention is called to the fact that in order to get trustworthy results with the conventional saponification method, the potassium hydroxide should be dissolved in absolute alcohol and the strength of the other alcohol used in the process should be 96 per cent.

To facilitate the work, when large numbers of samples have to be tested, 3.6 grams of the sample are operated on and an alcoholic solution of potassium hydroxide is used of such a strength that 20 to 22.5 c.c. neutralise 20 c.c. of $N/2$ sulphuric acid. Reference can then be made to a table from which the acidity or ether number is read off.

L. DE K.

Estimation of Methyl Anthranilate in Essential Oils. By ALBERT HESSE and OTTO ZEITSCHEL (*Ber.*, 1901, 34, 296—300).—The oil is dissolved in 2—3 times its weight of dry ether, the solution cooled to at least 0°, a mixture of concentrated sulphuric acid and ether (1:5 by vol.) added until no further precipitate of methyl anthranilate sulphate is formed, and the precipitate filtered and washed thoroughly with dry ether. If it is small in amount, it is dissolved in water, and the sulphuric acid titrated with $N/2$ potassium hydroxide and phenolphthalein; the solution is heated with excess of $N/2$ alcoholic potassium hydroxide, and the excess of alkali titrated with $N/2$ sulphuric acid. Each 1 c.c. of alkali used in the hydrolysis corresponds with 0.0755 gram of methyl anthranilate; if the alkali used in the hydrolysis is less than half that used in the first titration, bases not susceptible of hydrolysis must also be present; they may be extracted with ether from the alkaline liquid after hydrolysis. From the residual liquid, the anthranilic acid can be obtained by evaporating, acidifying with acetic acid, and extracting with ether, and can be identified by its melting point, which remains unchanged when the substance is mixed with some pure anthranilic acid.

If the quantity of precipitate is larger, it is dissolved in water, and an aliquot part titrated as above; the bulk of the solution is freed from resinous matter by extraction with light petroleum, and neutralised with sodium carbonate; the precipitate then formed is dissolved in ether, and saturated with dry, gaseous hydrogen chloride. Methyl anthranilate hydrochloride is precipitated, and can be identified by its melting point; other bases may remain dissolved in the acid ethereal solution.

Experiments were made with mixtures containing 5, 1, and 0.25 per cent. of methyl anthranilate; the amounts found were 5.10, 1.04,

and 0.227 per cent. A sample of oil of neroli was found to contain about 0.6 per cent. of the ester. C. F. B.

Estimation of Urea. By HUGO POLLAK (*Pflüger's Archiv*, 1901, 83, 232—240).—Schöndorff's method of estimating urea is compared with that introduced by Freund and Töpfer; the latter method gives rise to some loss. W. D. H.

Some Colour Reactions of Citrophén, Phenacetin, Methacetin, Acetanilide, and Exalgin with Potassium Permanganate. By J. J. M. MAAS (*Chem. Centr.*, 1900, ii, 1215; from *Ned. Tydschr. Pharm.*, 12, 321).—If a trace of these compounds is mixed with 1 c.c. of *N* sodium hydroxide and a few drops of a 1 per cent. solution of potassium permanganate are added, a violet colour appears which turns blue and then green; on supersaturating with sulphuric acid, the colour turns red and rapidly fades. If sodium carbonate is substituted for the hydroxide, citrophén [citrotriphenetidine] reacts at once, phenacetin and methacetin [*p*-acetylanisidine] slowly, acetanilide and exalgin [methylacetanilide] not at all; on substituting sodium hydrogen carbonate, only citrophén gives a reaction. An acid solution is only affected by citrophén and phenetidine. The other compounds decolorise an acid solution of potassium permanganate after some time. L. DE K.

A New Artificial Colouring Matter in Wine and the Detection of Orchil, Cochineal, Phytolacca, and Beet root Red in Wine. By J. BELLIER (*Chem. Centr.*, 1900, ii, 1296—1297; from *Ann. Chim. anal. appl.*, 5, 407).—Dyes more difficult to detect than those formerly used are now often added to wine. Such a one is the so-called "Orchil Red," a mixture of orchil with indigo-carmin. When present in wine, it gives a colourless filtrate with mercuric acetate, and is not taken up by amyl alcohol, but it betrays its presence by a bright red colour on adding excess of borax or ammonia. It may be separated from the wine by adding albumin, or a feebly ammoniacal casein freed from fat. The precipitate is washed, pressed between filter paper, and while still moist shaken with 86 per cent. alcohol containing 3—4 per cent. of ammonia. The solution is evaporated to dryness, the residue dissolved in water, re-evaporated, and extracted with 95 per cent. alcohol. A red alcoholic solution and a blue residue, soluble in water, are obtained.

A general scheme for the examination of a wine for artificial colouring matters may take the following form. The wine is first tested by mercuric acetate and magnesia for coal-tar dyes. A reagent is then prepared with 5 grams of mercuric oxide, 10 grams of ammonium sulphate, 15 c.c. of ammonia of sp. gr. 0.92, and water to 50 c.c. Ten c.c. of the wine are shaken with 1 c.c. of this reagent, or more if the wine is strongly acid. Pure wines become colourless, yellowish, or grey; wines containing a dye give a red filtrate. A very sensitive reagent consists of two solutions, the first containing 10 grams of mercuric chloride, 5 grams of ammonium chloride, and 100 c.c. of water, the second of 10 c.c. of glacial acetic acid, 65 c.c. of water, and 25 c.c. of ammonia (0.92). Ten c.c. of the wine are shaken with 1 c.c. of the

first, then 1 c.c. of the second added, shaken again, and filtered. The colour of the filtrate is to be observed immediately, as it becomes orange-yellow later. For further testing, the filtrate is halved, one part treated with lime water, shaken, and half an hour later acidified with acetic acid; a red coloration indicates orchil or cochineal; the latter gives a red filtrate, orchil a colourless one, when 10 c.c. of the wine are shaken with 0.2—0.3 gram of stannous chloride and excess of calcium carbonate. The other half is treated with ignited magnesia and then acidified with acetic acid; beet-root gives a red filtrate; phytolacca a colourless one.

M. J. S.

Adulteration of Saffron; "Saffron Essence." By WILHELM FRESenius and LEO GRÜNHUT (*Zeit. Nahr.-Genussm.*, 1900, 3, 810—819).—A report on the adulteration of two samples of saffron, and of a liquid which had apparently been used for adulterating the second sample. In analyses of this kind, it is not sufficient to merely estimate the moisture and the ash and call the balance dry saffron, but a complete analysis of the mineral matter should be made by operating on the sample itself and not on the ash.

The result of the analysis of the first sample was as follows: Crystallised magnesium sulphate, 25.5; crystallised borax (10 aq.), 8.23; crystallised normal sodium borate (8 aq.), 17.49; and saffron, 48.78 per cent.; total mineral adulterants, 51.32 per cent. The second sample showed: potassium nitrate, 12.94; crystallised normal potassium borate, 20.86; crystallised normal sodium borate, 6.41; sodium hydroxide, 3.21; saffron, 56.58 per cent.; total mineral adulterants 43.42 per cent. In this calculation, it was assumed that in the presence of much free alkali normal sodium borate crystallises with four instead of eight and neutral potassium borate with three instead of four H_2O . It will be readily seen that, owing to these salts retaining part of the water at 100°, and to absorption of carbon dioxide during the drying, an estimation of moisture in the ordinary way would have given erroneous results. The ash would also not have represented the true mineral matter. The result of the analysis of the so-called "Saffron Essence," of which full analytical details are given, was as follows: water, 46.57; crystallised borax, 16.87; potassium hydroxide, 8.94; potassium nitrate, 10.03; saffron (extract), 0.40; sucrose, 9.91; dextrose, 1.65; and dextrin (by difference), 5.63 per cent. The authors are not aware for what purpose it is intended to be used.

L. DE K.

Cryoscopic Testing of Medicines. By ALEXANDER VON POHL (*Chem. Centr.*, 1900, ii, 1294; from *Pharm. Post*, 33, 621—623).—The cryoscopic method of testing medicines is recommended as an addition to the usual tests, and is especially useful in the case of solutions of alkaloids, as it involves no loss of material.

E. W. W.

Characteristics of Ovalbumin, Serum-albumin (Sérines), and Serum-globulin. By GABRIEL GUÉRIN (*J. Pharm.*, 1900, [vi], 12, 465).—When 15—20 per cent. of formaldehyde is added to a solution of serum-albumin, no precipitate is produced, and after a certain time the liquid loses the property of being coagulated by heat, or by nitric acid in the cold. A solution of ovalbumin, when similarly treated,

gives no precipitate on heating, but is coagulated by nitric acid in the cold. Formaldehyde produces a gelatinous precipitate in strong solutions of serum-globulin, and a flocculent precipitate in dilute solutions.

H. R. LE S.

Simple and Rapid Estimation of Humic Acid. By HUGO BORNTÄGER (*Zeit. anal. Chem.*, 1900, **39**, 790—791).—The method depends on the oxidation of humic acid by a hypochlorite. A standard humic acid solution is prepared by boiling 10 grams of Cassel brown 1a (which may be assumed to contain 98 per cent. of humic acid) with 3 grams of sodium carbonate and 100 c.c. of water for an hour, and diluting to a litre. Ten c.c. of this solution, acidified with 3 c.c. of concentrated hydrochloric acid, is employed to standardise a clear solution of bleaching powder (about 20 grams per litre), or one of sodium hypochlorite, which is added from a burette until the colour is destroyed. The substance to be assayed is then treated in exactly the same manner. M. J. S.

Analysis of Peat. By HUGO BORNTÄGER (*Zeit. anal. Chem.*, 1900, **39**, 694—698).—Peat varies greatly in composition and physical properties. Young peat is pale in colour, bulky, capable of absorbing water like a sponge, and consists mainly of vegetable fibre, but peat some centuries old, is black, much denser (3—7 times), absorbs scarcely any water, is very rich (40—50 per cent.) in humic acid, and contains from 2 to 5 times as much nitrogen as young peat. Contrary to the practice of French analysts, the author regards the estimation of the humic acid apart from the fibre as essential to a knowledge of the value of any specimen to the agriculturist or distiller. If the peat is to be used as fuel, its calorific efficiency should also be estimated. To estimate the humic acid and fibre, 1—2 grams of the peat are boiled for an hour with 5 grams of sodium carbonate and 200 c.c. of water, the fibre collected on a weighed filter, and the humic acid precipitated by acidifying the brown filtrate with hydrochloric acid and boiling. The precipitate is collected on either a paper or asbestos filter and dried at 105°. Nitrogen is present, partly as proteid, partly as ammonium humate; the total amount is estimated by Kjeldahl's process, the ammonia by distilling with aqueous sodium hydroxide either the peat itself or a sulphuric acid extract thereof. Water and ash are estimated by the usual methods; a complete analysis of the ash is almost valueless, since it consists chiefly of sand with calcium and iron compounds, whilst potash and phosphoric acid are almost entirely absent. Earth wax (0.5—1 per cent.) may be estimated by extraction with ether, but the information serves no useful purpose. M. J. S.

General and Physical Chemistry:

Determination of the Refractive Power as a Method for the Investigation of the Composition of co-existing Vapour and Liquid Phases. By E. H. J. CUNAEUS (*Zeit. physikal. Chem.*, 1901, **36**, 232—238).—The author has determined the refractive power of various mixtures of carbon dioxide and hydrogen, and finds that the numbers obtained almost coincide with the values calculated from the refractive powers and the quantities of the two gases, thus confirming the observation of Ramsay and Travers (*Abstr.*, 1898, ii, 273). The small differences between the calculated and observed figures can be explained by the deviations which gas mixtures show from Amagat's density rule.

The refractive power has been applied to determine the quantities of ether and acetone present in vapour which is in contact with liquid mixtures of varying compositions of the two ingredients. The vapour phase is always richer in ether than the liquid. Small quantities of ether mixed with much acetone cause greater differences in the composition of the vapour and liquid phases than little acetone added to much ether.

Van der Waals' formula, $1/p \cdot dp/dx_v = x_v - x_l/x_v(1 - x_v)$, connecting the composition of the vapour and the liquid, and the pressure (x_v, x_l, p), is only applicable when the quantity of ether or acetone is small. The deviation is possibly due to the formation of a thin film of liquid on the glass plates of the apparatus, thus giving rise to a false observation. The author calculates that the thickness of this film is 0.00083 mm. for ether, and 0.00449 mm. for acetone. J. McC.

Spectrum of the more Volatile Gases of Atmospheric Air which are not Condensed at the Temperature of Liquid Hydrogen. By GEORGE D. LIVEING and JAMES DEWAR (*Proc. Roy. Soc.*, 1901, **67**, 467—474).—Tubes showing the spectra of hydrogen, helium, and neon, as well as many less brilliant rays of unknown origin, have been examined, and the wave-lengths of all rays sufficiently strong to be seen easily or photographed with an exposure of 30 minutes have been approximately measured and tabulated. Analysis of the gas showed conclusively that hydrogen exists in sensible proportion in the earth's atmosphere. The spectrum of the volatile residue of air has been compared with that of the more volatile part of gas from the Bath spring. The latter, even if primarily derived from the atmosphere, seems to have undergone some sifting, which has affected the relative proportions of helium and neon.

As the mixture of gas investigated probably included portions of the gases that pervade interplanetary and interstellar space, the authors looked in the spectra for the prominent nebular, coronal, and auroral rays. The nebular lines were not present, and the coincidence of the coronal lines is doubtful. Several lines, however, in the spectra examined seemed to coincide with certain auroral lines. J. C. P.

Rotation Dispersion of Malic Acid. By BENEDICT WORINGER (*Zeit. physikal. Chem.*, 1901, **36**, 336—357).—In view of the anomalies of rotation in the case of malic acid, careful determinations were made for various solutions at 20°. In general, the results are of the same nature as those of Nasini and Gennari (*Abstr.*, 1896, ii, 285), but the actual numbers are considerably different, being in general higher. A curve of density against concentration is given, its accuracy being rendered probable by the fact that extrapolation leads to correct values for the density of water and of pure malic acid. Curves for specific rotation against concentration are approximately straight lines of the form $\alpha = A - Bq$, where q is the percentage of water. The values for the constants are calculated, and from them tables are constructed for the rotation at all concentrations for light of various wave-lengths. At high concentration, the solutions become laevorotatory for all rays examined, inactivity being obtained at the following values of q : red ($\lambda = 665.9$), 64.96; green ($\lambda = 533.0$), 74.02; dark blue ($\lambda = 448.2$), 86.56, but there is no concentration at which complete achromatism obtains. At the value $q = 78$, the lines for red and yellow cut, so that about this dilution anomalous dispersion is obtained, but the author does not confirm Nasini's observations of further anomalies. The variation of rotation with wave-length is in accord with the Boltzmann formula, $\alpha = A/\lambda^2 + B/\lambda^4$, and the values of the constants were calculated.

The form of surface representing rotation as a function of both wave-length and dilution is considered, and from it are deduced the results that for wave-lengths less than that of the ultra-violet line L, the rotation is positive at all concentrations, and that for no wave-length is it negative at all concentrations.

L. M. J.

Molecular Rotation of Ethyl *n*-Acyl-*l*-malates. By HANS REITTER (*Zeit. physikal. Chem.*, 1901, **36**, 129—167. Compare *Abstr.*,

| | B. p. | Pressure in mm. Hg. | $d_{20}^{20}/4^\circ$. | $[\alpha]_D^{20}$ | $[M]_D^{20}$. | Product of asymmetry $\times 10^6$. |
|--|--------------|---------------------------|-------------------------|-------------------|----------------|--|
| Ethyl acetyl- <i>l</i> -malate..... | 141.2—141.4° | 13 | 1.1169 | -22.60° | -52.43° | 17 |
| Ethyl propionyl- <i>l</i> -malate..... | 150.6 | 12 | 1.0926 | -22.79 | -56.06 | 0 |
| Ethyl <i>n</i> -butyryl- <i>l</i> -malate..... | 156 | 12 | 1.0735 | -22.75 | -59.15 | 0 |
| Ethyl <i>n</i> -valeryl- <i>l</i> -malate..... | 176—177 | 19 | 1.0551 | -21.38 | -58.56 | 11 |
| Ethyl <i>n</i> -hexoyl- <i>l</i> -malate..... | 182—182.6 | 17 | 1.0420 | -20.30 | -58.46 | 26 |
| Ethyl <i>n</i> -heptoyl- <i>l</i> -malate..... | 191.6—192.2 | 15—16 | 1.0289 | -19.30 | -58.27 | 44 |
| Ethyl octoyl- <i>l</i> -malate..... | 199.4 | 15 | 1.0162 | -18.21 | -57.53 | 61 |
| Ethyl pelargonyl- <i>l</i> -malate..... | 206.8—208.4 | 14—15 | 1.0073 | -17.24 | -57.17 | 77 |
| Ethyl decoyl- <i>l</i> -malate..... | 217.2—217.6 | 13—14 | 1.0011 | -16.61 | -57.14 | 91 |

1895, ii, 251).—The *n*-acyl esters were obtained by the action of the acid chlorides on ethyl *l*-malate, and purified by distillation under reduced pressure. The table on p. 214 contains the physical properties of the esters examined.

The results are at variance with Guye's hypothesis, according to which the rotatory power of a substance is proportional to its product of asymmetry.

In this homologous series, the molecular rotation rises to a maximum, reached at the butyryl derivative, then remains practically constant, showing, however, a slight progressive descent. A similar regularity has been observed in other homologous series by Tschugaeff (*Abstr.*, 1898, ii, 274, 495). J. McC.

Secondary Radio-activity of Metals. By HENRI BECQUEREL (*Compt. rend.*, 1901, 132, 371—373. Compare *Abstr.*, 1900, ii, 126).—The more penetrative rays emitted by extremely active radium preparations induce a radiation in objects of lead or aluminium subjected to their influence; the induced rays are less penetrative than those emitted by the exciting substance, and resemble the secondary Röntgen rays discovered by Sagnac. The phenomenon appears to be analogous to that of fluorescence or phosphorescence. G. T. M.

Laws of Transparency of Matter for X-Rays. By LOUIS BENOIST (*Compt. rend.*, 1901, 132, 324—327).—The examination of about 120 different elementary and compound substances has shown that the specific opacity of a substance for the X-rays is independent of its physical state and molecular condition. Thus, the opacity of water is the same as that of ice, whilst the different varieties of carbon or phosphorus behave alike. Benzaldehyde, also, has the same opacity as the polymeric benzoin. The specific opacity for X-rays is an additive property, since the observed opacities of compounds are found to be equal to the sum of the opacities of their constituent atoms. The specific opacity of the elements is an increasing function of, and approximately proportional to, their atomic weights.

N. L.

Specific Absorption of X-Rays by Metallic Salts. By ALEXANDRE HÉBERT and GEORGES REYNAUD (*Compt. rend.*, 1901, 132, 408—409).—The results published by Benoist (preceding abstract) were largely anticipated by the authors (*Abstr.*, 1899, ii, 586). It is found that the absorbent powers of solutions of the metallic nitrates and chlorides for X-rays increase with the atomic weight of the metal, when this quantity is plotted against the relative specific absorption, the curve obtained is approximately a rectangular hyperbola. This relationship is less simple in the case of bromides, iodides, or sulphates, the influence of the electro-negative ion becoming a disturbing factor when the radicle possesses a high molecular weight. In general, the absorbent power of compounds for X-rays varies directly with their molecular weight. In any compound it is the radicle of highest molecular weight which impresses its specific absorbent power most markedly on the substance, this being true for both positive and negative radicles. G. T. M.

Law of the Transparency of Matter for X-Rays. By LOUIS BENOIST (*Compt. rend.*, 1901, 132, 545—548. Compare preceding abstracts).—This communication contains a diagram of curves showing the connection between the atomic weights of the elements and their transparency towards X-rays of varying penetrative power. The experimental results when thus presented show the importance of taking into account the phenomenon of *radiochromism*, and the paper concludes with a criticism of the work of Hébert and Reynaud, who have made certain generalisations without considering this property of matter. G. T. M.

Action of Cathode Rays on Radio active Substances. By KARL A. HOFMANN, A. KORN, and EDUARD STRAUSS (*Ber.*, 1901, 34, 407—409. Compare this vol., ii, 19).—The sulphates of mercury, thallium, zirconium, lead, and thorium become fluorescent when exposed to the action of cathode rays emitted from a Hertzian apparatus, but do not acquire the property of acting on a photographic plate in the dark; thorium oxide, gadolinium oxide, and the rare earths from samarskite behave in a similar manner. Bismuth hydroxide and barium sulphate, niobate, titanate, and tungstate remain inert, and the bismuth preparations from pitchblende, which contain polonium but have lost their radio-activity on keeping for a long time, do not recover their property under the influence of the cathode rays.

The lead sulphate preparations from pitchblende, bröggerite, cleveite, samarskite, and uranium mica, which have lost their radio-activity by keeping, recover the property when exposed to the cathode radiations; the effect is most marked in the case of the specimens prepared from the fractions containing the most soluble chlorides, the induced activity persisting for several weeks. The lead sulphate derived from euxenite is not radio-active, but is rendered active by the cathode rays. These results justify the conclusion that the radio-active lead compounds contain a foreign element, and also that the radiations are related to the cathode rays and hence to the Röntgen rays. G. T. M.

Radio-activity Induced by Radium Salts. By P. CURIE and A. DEBIERNE (*Compt. rend.*, 1901, 132, 548—551. Compare Abstr., 1900, ii, 81, 83, 125, 126, 254, 586, 654).—The intensity of the induced radio-activity is greatly increased when the exciting material, contained in a small open vessel, is placed in the centre of an enclosed space. Sheets of various materials, when placed in different parts of this enclosure, become equally active after the same interval of time, even when placed behind leaden screens. When, however, these substances are placed either against the sides of the vessel containing the radio-active material or against the walls of the enclosure, it is found that their exterior surfaces only are rendered active. The activity induced in these sheets by a specimen of radio-active barium chloride containing a metal having an atomic weight of 174, is 8000 times as great as that exhibited by a plate of uranium of the same dimensions. The induced radio-activity persists when the plates are left in the enclosure from which the exciting material has been withdrawn, whereas it almost completely disappears in the course of a day when the materials are exposed to the air. When the substances to be rendered active

and the exciting material are placed in different enclosures connected by capillary tubes, the induced radio-activity is as intense as in the foregoing experiment. No induction can be observed, however, when the radio-active material is contained in a closed vessel, even although this is placed in the same enclosure as the plates under investigation. These results were produced to the same extent by the chloride, sulphate, and carbonate of radio-active barium, and also by actinium compounds; polonium salts, on the contrary, do not induce radio-activity. The induction is probably brought about by the action on the air of certain rays readily absorbed by this medium, the radio-activity being transmitted through the air from the exciting material to the experimental plates. The rate of increase in the radio-active intensity becomes greater as the enclosure is made smaller, the induced activity ultimately reaching a maximum value which depends on the original radio-activity of the exciting material.

G. T. M.

Influence of the Medium on the Photochemical Effect in Silver Bromide Emulsions, and Photochemical Induction. By RICHARD ABEGG [and CL. IMMERWAHR] (*Monatsh.*, 1901, 22, 88—94).—Following the investigations of Luggin (*Abstr.*, 1897, ii, 470) and Luther (*Abstr.*, 1900, ii, 181, 253), the author suggests that the state of equilibrium is never reached in the ordinary process of obtaining a photographic negative, because (1) the exposure is too short, and (2) the halogen set free from the silver salt does not attain the equilibrium potential, owing to the fact that it is removed either by reacting with the medium, for instance, gelatin, or by diffusion. Gelatin probably owes its use as a "chemical sensitiser" to the readiness with which it interacts with halogen. On the other hand, the diffusion of the halogen would be hindered by the gelatin. The influence of diffusion is demonstrated by exposing two similar gelatin silver bromide plates, the one with the gelatin layer, the other with the glass towards the source of light. The action on the bromide was less in the latter case, as the close opposition of the glass to the gelatin prevented the diffusion of the halogen, and consequently reduced the action of the light.

K. J. P. O.

Luminosity obtained with certain Organic Compounds. By RAPHAEL DUBOIS (*Compt. rend.*, 1901, 132, 431—432).—Many organic compounds, when warmed with alcoholic potassium hydroxide, yield solutions which are luminous in the dark; in some cases, this result is attained even with the cold reagent. The essences of camomile, rosemary, cumin, rose, and *Illicium anisatum* behave in this manner. The best result is obtained with æsculin; this glucoside yields a solution which remains luminous during a whole night, the luminosity increasing when the solution is shaken in the presence of atmospheric air; the fluorescence is destroyed by adding water to the alkaline alcoholic solution. Even in this case, however, the luminosity is far less than that obtained with solutions of marine photobacteria.

G. T. M.

The Electrical Arrangements of the Chemical Laboratory of the Mining School at Clausthal. By FRIEDRICH W. KÜSTER (*Zeit. anorg. Chem.*, 1901, 26, 167—174).—A description of a simple,

inexpensive, and flexible arrangement of a battery of accumulators intended to be charged from an electric lighting circuit at 110 volts and to furnish a supply of electricity for experimental purposes at any pressure from 4 to 96 volts. The advantages of the arrangement are, that all the cells are discharged simultaneously and equally, and the loss of energy in charging is reduced to a very small quantity.

T. E.

Gas Polarisation in Lead Accumulators. By C. J. REED (*J. Physical Chem.*, 1901, 5, 1—16).—In order to explain why with lead electrodes electrolysis does not take place with E.M.F.'s below 2 volts, hydrogen not being liberated until 2·3 volts is reached although the electrolyte is decomposed between platinum electrodes at 1·7 volts, Nernst and Dolezalek have considered that the E.M.F. required for the liberation of hydrogen is dependent on the occluding capacity of the metal employed (*Abstr.*, 1900, ii, 164). The author shows, however, that the anomaly does not exist, for hydrogen is liberated between lead electrodes with an E.M.F. of 0·38 volt, whilst a steady current could be obtained with 0·01 volt. Previous investigators had not used lead electrodes, but by waiting for a constant value had delayed observation until the anode had become coated with a film of lead sulphate. For the theoretical investigation also, the question must not be treated merely as a liberation of hydrogen, but the total energy absorbed by the actual chemical changes must be considered. When the anode is converted into lead sulphate, the reaction proceeds with evolution of hydrogen and formation of lead peroxide necessitating 1·73 volts, when the anode is lead peroxide, an E.M.F. of 1·95 volts is required for the production of hydrogen peroxide and 2·23 volts for the formation of persulphuric acid. If the cathode is of lead sulphate, somewhat higher values are required, and with acid of sp. gr. 1·20 the values must be increased by 0·08 volt. These values are in good accord with experimental determinations.

L. M. J.

Diminution of Cathodic Depolarisation by Potassium Chromate. By ERICH MÜLLER (*Zeit. Elektrochem.*, 1901, 7, 398—405).—The yield of chlorate in the electrolysis of a solution of an alkali chloride is much increased by the addition of a little potassium chromate to the liquid. A catalytic acceleration of the oxidation of hypochlorite to chlorate would reduce the concentration of the former in the solution, and also the quantity of oxygen escaping at the anode, whereas in reality the opposite effects are observed. The action of the chromate really consists of a diminution of reduction at the cathode. With a cathode of chromium (in a solution of potassium iodate), about 22 per cent. of the current was employed in reduction, whilst the addition of a little chromate diminished this to about 11 per cent. The diminution of the reduction does not, therefore, appear to be due to a specific action of chromium. The phenomena observed are all explicable on the supposition that a thin deposit of the oxide, Cr_2O_3 or $\text{Cr}_2\text{O}_3\cdot\text{CrO}_3$, is formed on the cathode, which prevents the reducible substance (hypochlorite, iodate, nitrate) from coming into immediate contact with it. With a platinum cathode, for example, in

a solution of potassium iodate, 50—60 per cent. of the current produced reduction; the addition of a little potassium chromate to the solution diminished this to 3 to 6 per cent. The cathode was then washed and used in a fresh solution of iodate without chromate, when 27—33 per cent. of reduction was observed. A slight yellow film containing chromium can be detected on such a cathode.

T. E.

Studies on Cathodic Polarisation and Depolarisation. By ERICH MÜLLER (*Zeit. anorg. Chem.*, 1901, 26, 1—89).—In electrolytic reduction, the nature of the metal forming the cathode often exercises a great influence on the results obtained. The potential difference required to produce visible formation of hydrogen bubbles is always greater than the potential difference of the hydrogen electrode under similar conditions, and the excess required depends on the nature of the metal. The author finds the excess *P.D.* required to produce the smallest visible quantity of hydrogen from normal sulphuric acid to be as follows: platinised platinum, 0.01 volt; smooth platinum, 0.07 volt; gold, 0.06 volt; silver, 0.05 volt; copper, 0.03 volt; nickel, 0.03 volt; mercury, 0.42 volt; palladium, 0.24 volt; tin, 0.43 volt; lead, 0.35 volt. The values are smaller than those obtained by other observers, and depend largely on the nature of the metallic surface, smooth surfaces giving higher values than rough ones. With mercury, the results were very variable and uncertain. It is interesting to note that, with the exception of palladium, the excess *P.D.* is very small for metals which are more negative than hydrogen, whilst tin and lead, which are more positive than hydrogen by 0.41 and 0.28 volt respectively, give excesses of about the same amounts.

Between a solution of any reducible substance and a metallic electrode, there exists a definite potential difference at which reduction should begin, provided that there is no retardation analogous to that observed in the evolution of hydrogen at metallic surfaces. It is therefore conceivable that the *P.D.* required for the reduction of a substance might be greater than that at which hydrogen is evolved from one metal, but less than that at which it is evolved from another. Reduction would then be observed when the second metal is used as cathode, but not with the first. By a method similar to that used for the determination of discharge potentials, the author has measured, in several cases, the lowest E.M.F. at which reduction proceeds moderately fast, that is, with a velocity comparable with the velocity of hydrogen discharge needed to produce visible gas bubbles. He finds that an excess over the theoretical potential difference (obtained from an oxidation cell) is required, just as in the discharge of hydrogen, and that this excess depends on the nature of the metal used. In 0.01*N* solutions of sodium hydroxide, potassium iodate and bromate are much reduced before hydrogen begins to be evolved on platinum cathodes, and in the case of the iodate, reduction takes place more readily with platinised than with smooth platinum cathodes. With potassium nitrate, reduction and evolution of hydrogen begin almost simultaneously, whilst with sodium chlorate, hydrogen is evolved first, and therefore no reduction takes place. With cathodes of iron,

mercury, and zinc, the reduction of potassium nitrate begins before the evolution of hydrogen. This was confirmed by electrolysis of normal solutions of potassium nitrate on a larger scale, when it was found that about 15 per cent. of the cathodic hydrogen was used in reduction with a platinised platinum cathode, 76 per cent. with smooth platinum, 97.5 per cent. with iron, and 97 per cent. with zinc. The E.M.F. required for reduction at an iron cathode is, however, about 0.3 volt less than at a zinc cathode. Very similar results were obtained with potassium nitrite, which is, however, less readily reduced than the nitrate at a platinum cathode, and more readily at cathodes of iron and zinc. Copper and mercury gave results similar to iron and zinc respectively. Hydroxylamine and hydrazine are much more readily reduced than either nitrate or nitrite; they cannot therefore be formed as intermediate products of the reduction.

Anomalous results were obtained with sodium chlorate. When a gradually increasing E.M.F. is applied to a neutral solution of this salt, a sensible current passes before hydrogen begins to be evolved only when the cathode is of iron or cobalt; with other metals (platinum, gold, silver, copper, nickel, tin, zinc, lead, and cadmium) the passage of the current corresponds with the liberation of hydrogen. Sodium chlorate should therefore be reduced at cathodes of iron and cobalt. As a matter of fact, it is only reduced at a cathode of iron. Further, the evolution of hydrogen from cathodes of zinc and mercury requires a higher E.M.F. than from iron; the author supposes that the fact that no reduction takes place with these metals must be due to some special catalytic action of iron. According to the theory of oxidation cells, a substance should be the more readily reduced the smaller the concentration of the OH ions in the solution; this holds for potassium iodate, which is much more reducible in acid than in alkaline solution.

Reduction in general takes place more readily at a rough than at a smooth surface.

Reduction may be retarded or prevented by the formation of a deposit on the cathode which acts as a diaphragm. The behaviour of potassium chromate is fully considered in this connection (see preceding abstract).
T. E.

Dielectric Constant of some Gases and Vapours and its Dependence on Temperature. By KARL BÄDEKER (*Zeit. physikal. Chem.*, 1901, **36**, 305—335).—The dielectric constants were determined in a manner essentially similar to that employed by Nernst (*Abstr.*, 1894, ii, 437) and Philip (*Abstr.*, 1898, ii, 9), the values being obtained by comparison with air or hydrogen. The following gases were examined, carbon disulphide from 85—129°; sulphur dioxide, 10.3—103.3°; ammonia, 18.4—108.4°; water, 140—148.6°; hydrogen chloride, 84—106°; methyl alcohol, 93.2—149.5°; ethyl alcohol, 112.4—144.8°, and nitrogen peroxide, 42.5—92.1°. The validity of the Clausius-Mossotti formula, $(k-1)/(k-2)d = \text{constant}$, was examined, and it was found that in general the formula does not hold, and that also the Maxwell relation, $k = \mu^2$, is not valid, whilst the departure from the Clausius law is such that at high temperatures the dielectric constant approximates to the square of the refractive index.
L. M. J.

Conductivity produced in Gases by the Motion of Negatively charged Ions. By JOHN S. TOWNSEND (*Phil. Mag.*, 1901, [vi], 1, 198—227).—Plates of aluminium and brass at different potentials were exposed to the influence of Röntgen rays, and the current produced was measured under various conditions of pressure, potential difference, &c. The pressure varied from 4.13 mm. to 0.171 mm., and each set of experiments was made with distances between the plates of 0.5, 1, and 2 centimetres. Curves are drawn for current against potential difference per centimetre, and these show that the current at first varies but slightly with potential difference, but for higher values of the latter it increases very rapidly, and that the curves are steeper the greater the distance between the plates. These results are completely explained, quantitatively as well as qualitatively, by the theory developed by the author, which assigns the conductivity to the negative ions, these, in their motion between the plates, producing by collision other ions. It is shown that the negative ions must be far smaller than the ordinary molecules or the positive ions, and their velocity of agitation is far greater than that of air molecules. Incidentally, it is estimated that the energy required to ionise a molecule is about 10^{-11} ergs. It is also shown that the experiments of Stoletoff (*J. Phys.*, [ii], 9), are also in accord with those of the author and with the theoretical assumptions, which are further in agreement with the conclusions derived from the diffusion of the ions (this vol., ii, 3).

L. M. J.

Electrical Conductivity of Solutions of the Alkali Iodates, and a Formula for the Calculation of the Conductivity. By FRIEDRICH KOHLRAUSCH (*Sitzungsber. Akad. Wiss. Berlin*, 1900, 1002—1008. Compare Kohlrausch and Maltby, *Abstr.*, 1900, ii, 61; this vol., ii, 82).—The exact conductivity determinations previously made for the chlorides and nitrates of potassium, sodium, and lithium have been supplemented by similar determinations for the iodates of the same metals at 18°. The results are contained in the following table:

| <i>m.</i> | KIO ₃ . | NaIO ₃ . | LiIO ₃ . |
|-----------|--------------------|---------------------|---------------------|
| 0.0001 | 97.64 | 76.69 | 66.66 |
| 0.0002 | 97.34 | 76.44 | 66.43 |
| 0.0005 | 96.72 | 75.83 | 65.87 |
| 0.001 | 96.04 | 75.19 | 65.27 |
| 0.002 | 95.04 | 74.30 | 64.43 |
| 0.005 | 93.19 | 72.62 | 62.89 |
| 0.01 | 91.24 | 70.86 | 61.23 |
| 0.02 | 88.64 | 68.56 | 59.05 |
| 0.05 | 84.06 | 64.43 | 55.26 |
| 0.1 | 79.67 | 60.46 | 51.50 |
| 0.2 | 74.34 | 55.45 | 46.88 |

To express the alteration of the conductivity with the dilution, the author advocates the equation $(\lambda_{\infty} - \lambda)/\lambda^p = c.m^{\frac{1}{2}}$, where λ is the conductivity at the equivalent concentration m , c is a constant, and p is an exponent which varies from salt to salt (compare the formulæ of Rudolphi, *Abstr.*, 1895, ii, 490; and van't Hoff, *Abstr.*, 1896, ii, 145). When tested by the experimental results recorded in this and the earlier paper, the author's formula is found satisfactory up to $m=0.1$.

The values finally adopted for the ionic conductivities at infinite dilution are as follows :

| K. | Na. | Li. | Cl. | NO ₃ . | IO ₃ . |
|-------|-------|-------|-------|-------------------|-------------------|
| 64.67 | 43.55 | 33.44 | 65.44 | 61.78 | 33.87. |

J. C. P.

The Amperemanometer. By ANDRÉ JOB (*Zeit. Elektrochem.*, 1901, 7, 421—423).—The instrument is similar to that described by Bredig and Hahn (*ibid.*, 259. See also this vol., ii, 83). It consists essentially of an ordinary voltameter ; the mixture of hydrogen and oxygen evolved is, however, not collected, but is allowed to escape through a capillary tube. The pressure thus produced in the apparatus, which is nearly proportional to the volume of gas escaping in unit time, and therefore to the current, is measured on a manometer which is graduated in amperes. Spirling and frothing are prevented by a layer of petroleum on the surface of the liquid, and the temperature correction is made by slipping a platinum wire into the capillary tube to a depth which is marked on the tube for each temperature.

T. E.

Thermoelectric Behaviour of some Oxides and Metallic Sulphides. By EDMUND VAN AUBEL (*Ann. Phys.*, 1901, [iv], 4, 416—419).—In a recent paper (*Ann. Phys.*, 1900, [iv], 2, 266), Abt arranged a number of metallic oxides and sulphides in the order of their thermoelectric efficiency, and drew the conclusion that the members of this series followed the thermoelectric summation law which holds for metals. The author takes several sets of numbers given by Abt, and shows that the latter's conclusion is not justified by his experimental data.

J. C. P.

Electro-affinity of the Metals. By HARRY M. DAWSON and JOHN MCCRAE (*Zeit. anorg. Chem.*, 1901, 26, 94—103).—Abegg and Bodländer (Abstr., 1899, ii, 542) have pointed out that weak ions (atoms or groups of atoms which possess but little affinity for an electron) are those which most readily combine with an electrically neutral molecule to form a complex ion. The authors refer to their experiments on the complex ammonia compounds of copper, nickel, cadmium, and zinc, which show that the ions of these metals combine equally readily with 4 mols. of ammonia. Since the E.M.F.'s required to separate the ions of the above-mentioned metals from their charges are respectively -0.34 , $+0.23$, $+0.38$, and $+0.74$ volt, they should, according to Abegg and Bodländer, possess very different tendencies to combine with ammonia. Furthermore, the results so far obtained by the authors with the alkali metals are not in accordance with Abegg and Bodländer's generalisation. Experiments on the partition of ammonia between chloroform and solutions of silver chloride in ammonia show that the latter contain the compound $2\text{AgCl}, 3\text{NH}_3$.

T. E.

Reactions of Cobalt and Iron, and the Influence of Alcohols and other Organic Substances on the Electrolytic Dissociation of Salts in Aqueous Solution. By HUGO DITZ (*Chem. Zeit.*, 1901, 25, 109—112).—When a solution of a cobalt salt

is mixed with half its volume of glycerol, and a few drops of ammonia are introduced above the mixture, the ammoniacal layer is coloured an intense yellow. Since nickel does not interfere, even when present in considerable quantity, the reaction is a useful test for cobalt.

The addition of glycerol to a solution of ferric chloride produces a marked intensification of the colour; this effect (which is produced also by ethyl and methyl alcohols) is attributed to the diminished dissociation caused by the introduction of a substance with lower dielectric constant. In this connection, the author discusses Grassini's experiments (this vol., ii, 43); according to Grassini, the blue colour produced at the contact surface of alcohol and a mixture of cobalt chloride and potassium thiocyanate solutions is destroyed by hydrogen peroxide; the author shows that the colour is destroyed by the same volume of pure water, and explains the phenomena on dissociation lines. When an extremely dilute solution of cobalt sulphate is mixed with potassium thiocyanate and alcohol, no blue colour is observed unless a few cubic centimetres of ether are added, the ether presumably favouring the formation of the undissociated compound to which the blue colour is due. Acetone is quite as effective as a mixture of alcohol and ether. This delicate reaction may be used to detect cobalt in presence both of nickel and iron.

The part played by dissociation in these colour reactions is further illustrated by the discharge of the blue colour of alcoholic cobalt chloride solutions on the addition of water. J. C. P.

Depression of the Freezing Point in Aqueous Solutions of Electrolytes. By JAMES G. MACGREGOR (*Trans. Roy. Soc. Canada*, 1900, [ii], 6, Sect. III, 3—19. Compare this vol., ii, 8).—The value of many physical properties of dilute solutions of electrolytes may be expressed thus: $P = P_w + k(1 - \alpha)n + l\alpha n$, where P and P_w are the values of the property for the solution and for water respectively, n is the concentration, α is the ionisation coefficient, and k and l are constants. The author shows that the expression can be applied to the case of the freezing point, and that this knowledge may be used in obtaining approximate values for the depression of the freezing point per gram mol. by the undissociated, and per gram ion by the free ions. When δ represents the equivalent depression of the freezing point, the above equation becomes: $\delta = k + (l - k)\alpha$; if therefore the expression is applicable, the curve obtained by plotting equivalent depression against ionisation coefficient should at sufficient dilution become practically a straight line. Using the experimental data of Archibald (*Abstr.*, 1900, ii, 65), and Barnes (*Abstr.*, 1900, ii, 526), the author finds that for the more dilute solutions the differences between calculated and observed values are within the limit of experimental error. The above expression may also be extended to calculate the depression in solutions of more than one electrolyte. J. C. P.

A Proposal regarding the Definition of Thermal Capacity. By THEODORE W. RICHARDS (*Zeit. physikal. Chem.*, 1901, 36, 358—360).—A plea for a change in the calorie which would give a simpler connection with the erg. The suggestion is that the thermal unit

should be 10^7 ergs or 1 Joule, this being about $1/4.2$ of the present value. L. M. J.

Development of the Thermodynamical Potential in Terms of T and p in the Case of Compound Components. By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 1901, **36**, 216—224).—A mathematical paper not suitable for abstraction. J. McC.

The Specific Heat of Solutions. By KARL PUSCHL (*Monatsh.*, 1901, **22**, 77—87).—The specific heat of aqueous solutions of electrolytes has always a smaller value than would be the case if the water and the solute respectively exhibited the specific heats they possess in the free state. With increased dilution, this deviation increases until in some cases, if the specific heat of the water = 1, that of the solute becomes a negative quantity. The author suggests that the specific heat of the water in the solution has not its normal value, but that some part of the water (the "hydrate water") has the specific heat 0.5, that is, the specific heat of ice. Thus the specific heat of a solution of potassium hydroxide of the composition ($\text{KHO} + 30\text{H}_2\text{O}$) requires that $4\text{H}_2\text{O}$ should have this reduced specific heat, and the conclusion is drawn, therefore, that the hydrate, $\text{KHO} \cdot 4\text{H}_2\text{O}$, is present. As the dilution increases, the quantity of "hydrate water" increases, but in the case of sodium hydroxide reaches a maximum, and then decreases. K. J. P. O.

Specific Heat and Latent Heat of Fusion of Ethylene Glycol. By ROBERT DE FORCRAND (*Compt. rend.*, 1901, **132**, 569—571. Compare Abstr., 1900, ii, 527).—In a former communication, the author assumed that the molecular heat of ethylene glycol is 2.66 Cal. This assumption has now been verified by direct experiment on a sample of the compound melting at -11.5° . The specific heat of liquid glycol, determined for the following ranges of temperature, $139-13^\circ$, $59.6-13^\circ$, $9- -22.8^\circ$, was 0.6268, 0.5848, and 0.5365 respectively; in the last case, the compound was in a state of superfusion. These results correspond closely with the values calculated from the equation $Q = 0.54453t + 0.0005675t^2$, showing that the law of variation of the specific heat is not modified by the superfusion. The above data were employed in determining the latent heat of fusion of the compound, the specific heat of solid glycol being assumed to be 0.265 at temperatures near the melting point. The mean molecular heat of fusion of glycol as experimentally determined is 2.683 Cal. G. T. M.

Vapour Pressure of Ternary Mixtures. By FRANZ A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1901, **36**, 257—289).—A more extended and fuller treatment of the author's previous paper on the same subject (this vol., ii, 146). L. M. J.

Thermochemical Study of the Ammonio-aluminium Chlorides. By E. BAUD (*Compt. rend.*, 1901, **132**, 553—556. Compare this vol., ii, 161).—The ammonio-aluminium chlorides are stable in a dry atmosphere, the salt containing 18 mols. of ammonia, decomposing, however, at temperatures above 0° ; they are all decomposed by water; the compound, $\text{Al}_2\text{Cl}_6 \cdot 12\text{NH}_3$, has the following

thermochemical constants: heat of dissolution, 12·70 cal., and heat of formation, 268·23 cal., the heat evolved for each addition of 1 mol. ammonia being 22·35 cal.

The heats of dissolution and formation of the compound $\text{Al}_2\text{Cl}_6, 10\text{NH}_3$ are 18·10 and 245·23 cal. respectively, the heat generated in converting this substance into the preceding salt being 23·00 cal. The heats of dissolution and formation of the diammonio-salt are 97·45 and 82·28 cal. respectively, the conversion of this substance into the decammonio-salt being attended by a generation of 162·95 cal. The temperatures of decomposition of the di-, deca-, and duodeca-salts as calculated from thermochemical data are 1013° , $363\cdot6^\circ$, and $86\cdot4^\circ$ respectively; it is found experimentally that the decammonio-compound decomposes at 380° under atmospheric pressure, whereas the diammonio-salt distils without decomposition at 480° .

The heat of fixation of 1 mol. of water (gaseous) in the hydrate, $\text{Al}_2\text{Cl}_6, 12\text{H}_2\text{O}$, is 22·25 cal., a value corresponding with that determined for 1 mol. of ammonia in the case of the ammonio-analogue, $\text{Al}_2\text{Cl}_6, 12\text{NH}_3$.
G. T. M.

Alteration of Free Energy during the Formation of some Slightly Soluble Metallic Salts. By ARTHUR KLEIN (*Zeit. physikal. Chem.*, 1901, 36, 361—371).—The heat developed in certain reactions was calculated from determinations of the E.M.F. and its temperature coefficient (see Czepinski, Abstr., 1899, ii, 267). The following results were obtained: $\text{PbCl}_2 + 2\text{KBr(aq)} = \text{PbBr}_2 + 2\text{KCl(aq)}$, + 3560 cal.; $\text{PbBr}_2 + 2\text{KI(aq)} = \text{PbI}_2 + 2\text{KBr(aq)}$, + 5770 cal.; $\text{PbCl}_2 + 2\text{KI(aq)} = \text{PbI}_2 + 2\text{KCl(aq)}$, + 9330 cal.; $\text{PbCl}_2 + \text{K}_2\text{SO}_4(\text{aq}) = \text{PbSO}_4 + 2\text{KCl(aq)}$, - 2480 cal.; $\text{PbBr}_2 + \text{K}_2\text{SO}_4(\text{aq}) = \text{PbSO}_4 + 2\text{KBr(aq)}$, - 6040 cal.; $\text{PbI}_2 + \text{K}_2\text{SO}_4(\text{aq}) = \text{PbSO}_4 + 2\text{KI(aq)}$, - 11810 cal.; $\text{CuBr} + \text{KI(aq)} = \text{CuI} + \text{KBr(aq)}$, + 6495 cal.; $\text{AgCl} + \text{KBr(aq)} = \text{AgBr} + \text{KCl(aq)}$, + 4260 cal.; $\text{AgBr} + \text{KI(aq)} = \text{AgI} + \text{KBr(aq)}$, + 6310 cal.; $\text{AgCl} + \text{KI(aq)} = \text{AgI} + \text{KCl(aq)}$, + 10570 cal. Of these reactions, that between lead iodide and potassium sulphate proceeds in the reverse direction at temperatures below 8° , so that the reaction is endothermic or exothermic according to temperature.
L. M. J.

Heat of Combustion of Glucosides. By EMIL FISCHER and WOLF VON LOEBEN (*Sitzungsber. Akad. Wiss. Berlin*, 1901, 323—326.

| | Molecular heat of combustion. | | Molecular heat of formation. |
|----------------------------------|-------------------------------|--------------------|------------------------------|
| | Constant volume. | Constant pressure. | |
| α -Methylglucoside | 846·4 Cal. | 846·7 Cal. | 296·5 Cal. |
| β -Methylglucoside | 844·9 | 845·2 | 298·0 |
| α -Methylgalactoside | 839·4 | 839·7 | 303·5 |
| α -Methylmannoside | 842·6 | 842·9 | 300·3 |
| Salicin | 1523·0 | 1523·6 | 323·4 |
| Helicin | 1480·5 | 1480·8 | 297·2 |
| Triacetone-mannitol ... | 2003·0 | 2005·0 | 306·6 |

The heat of formation of salicin from dextrose and saligenin is

-0.4 Cal., whilst that of helicin from dextrose and salicylaldehyde is +4.0 Cal. The heat of formation of triacetone mannitol from its generators is 4.2 Cal.

G. T. M.

Thermochemistry of *o*-Chlorobenzoic Acid. By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1901, [iii], 25, 195—196).—The heat of dissolution of *o*-chlorobenzoic acid is 6.2 Cal., and its heat of neutralisation by sodium hydroxide 15.96 Cal., the latter being greater by 2.26 Cal. than is the case with benzoic acid. The heat of dissolution of the anhydrous sodium salt is 2.1 Cal., whilst its heat of formation is 18.87 Cal., all the substances concerned being in the solid state. The heat of formation of sodium benzoate is 17.4 Cal.; hence the introduction of a chlorine atom in the ortho-position increases the heat of combination of benzoic acid by 1.47 Cal.

N. L.

Thermochemistry of *o*-Iodobenzoic Acid. By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1901, [iii], 25, 196).—The solubility of *o*-iodobenzoic acid in water is too small to allow of its heat of dissolution being directly determined. Its heat of dissolution in sodium hydroxide solution is 9.48 Cal. The heat of dissolution of the anhydrous sodium salt is 2.96 Cal., and its heat of formation from the solid base and acid is 17.73 Cal. The latter is only 0.33 Cal. greater than the corresponding value for sodium benzoate (see preceding abstract).

N. L.

Molecular Heats of Compounds and the Law of Neumann-Joule-Kopp. By EDMUND VAN AUBEL (*Ann. Phys.*, 1901, [iv], 4, 420—421).—Certain compounds are quoted as exceptions to Meyer's generalisation (*Abstr.*, 1900, ii, 464). Thus in the case of silver bromide and potassium iodide the molecular volume is less than the sum of the atomic volumes, whilst the molecular heat is greater than the sum of the atomic heats. For mercurous and mercuric iodides, the molecular volume is greater than the sum of the atomic volumes, whilst the molecular heat is less than the sum of the atomic heats. The exceptional behaviour of iron-antimony alloys is also referred to.

J. C. P.

Heats of Solution, especially that of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$. By H. B. HOLLSBOER (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 467—469).—If the solubility of a compound increases with temperature, the theoretical heat of solution, that is, the heat of solution in a saturated solution, must be negative, and *vice versa*. Cadmium sulphate, $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, has a minimum of solubility at 15°, and the theoretical heat of solution should therefore be zero at this temperature; the following values were obtained from experimental determinations: 5°, +219 cal.; 10°, +165 cal.; 15°, +3 cal.; 20°, -620 cal.; 25°, -1221 cal. If the thermal capacity of a solution is equal to the sum of the thermal capacities of the constituents, the heat of solution should be independent of temperature, and it was found that, at the concentration $\text{CdSO}_4 + 22.5\text{H}_2\text{O}$,

the curves for the various temperatures all cut, a peculiarity which probably occurs with many other substances. L. M. J.

Liquefaction of a Mixture of Two Gases. Composition of the Liquid and of the Vapour. By PIERRE DUHEM (*J. Physical Chem.*, 1901, 5, 91—112. Compare Abstr., 1897, ii, 364).—The author discusses the effect of pressure on a mixture of two liquefiable gases at various temperatures, and shows that above a certain temperature, which depends on the composition of the mixture, the mass remains homogeneous, whatever be the pressure. There exist also limiting pressures for lower temperatures between which the mixture is in part liquid and in part vapour, but above and below which it is homogeneous. At these intermediate pressures, two cases may occur, (a) when there is *retrograde condensation*, and (b) when there is *retrograde vaporisation*. In the former case, when a certain pressure is reached, a drop of liquid is formed and this at first increases with the pressure and its mass rises to a maximum, but further increase of pressure causes it to diminish and ultimately disappear. In the second case, when pressure is applied to a homogeneous liquid mixture at a certain pressure, a bubble of vapour appears and the mass of this increases up to a maximum, then diminishes, and finally disappears.

These cases are fully discussed with relation to the Gibbs-Konowaloff point, the temperature, and the composition of the mixture in the gaseous and liquid phases. Curves are given showing the variation of the concentration in the two phases at various temperatures with increasing pressure. J. McC.

Compressibility of Solutions. By JOSEPH GUINCHANT (*Compt. rend.*, 1901, 132, 469—472).—Experiments with aqueous solutions of alcohol, acetic acid, isobutyl alcohol, acetone, sucrose, resorcinol, and carbamide show that up to a pressure of 4 atmos. the volume of the dissolved substance is independent of the pressure. It follows that the variation in volume which accompanies the simple dissolution of a substance in water must be attributed to a change in the state of aggregation of the solvent rather than to the volume occupied by the dissolved molecules. C. H. B.

Relative Bulk of Weak Aqueous Solutions of Certain Sulphates and their Constituent Water. By CHARLES M. PASEA (*Trans. Roy. Soc. Canada*, 1900, [ii], 3, Sect. III., 27—36).—Macgregor has shown that in the case of weak aqueous solutions of certain sulphates, the solutions have a smaller volume than the water which they contain would have in the free state. Continuing this investigation, the author has determined the specific gravity of dilute solutions of sodium, manganese, cadmium, and ferrous sulphates; contraction has been found in the last three cases, but only at certain concentrations. Summarising all results obtained by himself and other observers, the author points out that solutions of cadmium, cobalt, copper, ferrous, magnesium, nickel, and zinc sulphates exhibit contraction. No contraction has been observed in the case of ammonium, ammonium-aluminium, ammonium-iron, ammonium-sodium, beryllium, ferric, hydrogen-potassium, lithium, magnesium-potassium, potassium, potass-

ium-aluminium, sodium, and potassium-iron sulphates. It is noted that in the former of the two lists, every metal is bivalent. J. C. P.

Deductions from Capillary Phenomena. By ALBERT EINSTEIN (*Ann. Phys.*, 1901, [iv], 4, 513—523).—If γ represents the work to be done on a liquid in order to increase the surface by unit area, the author shows that the function $\gamma - T.d\gamma/dT$ is more suited than γ itself for the discovery of additive relationships. He deduces the expression $\Sigma c_a = v.\sqrt{\gamma - T.(d\gamma/dT)}. \sqrt{(1/K')}$, where c_a represents the characteristic number for an atom, v is the molecular volume, and K' is a constant. Taking $c_H = -1.6$, $c_O = 55.0$, $c_C = 46.8$, the values of Σc_a are calculated for a number of organic compounds, and a fair agreement is found with the values of Σc_a obtained from the above equation. J. C. P.

Combustion of Gases. By SIMEON M. TANATAR (*Zeit. physikal. Chem.*, 1901, 36, 225—226. Compare this vol, ii, 13).—When 6 volumes of electrolytic gas are mixed with 1 volume of propylene and the mixture sparked over water for some time, a diminution in volume takes place. This diminution corresponds with the volume of propylene equivalent to the oxygen contained in the mixture, according to the formula $C_3H_6 + 3O_2 = 3CO + 3H_2O$. The hydrogen, therefore, takes no part in the combustion. The mixture can be ignited at a jet and burns with a luminous flame.

When passed through a glass tube heated at one spot to redness, the mixture ignites and the flame travels back a distance depending upon the rate of the gas current. The gas resulting from this combustion contains only carbon monoxide, hydrogen, propylene, and oxygen. The propylene alone takes part in the combustion, and part of the oxygen escapes combination because it has not time to unite with the excess of hydrogen and propylene at the proper temperature. J. McC.

Dependence of Hydrolysis on Temperature. By THORVALD MADSEN (*Zeit. physikal. Chem.*, 1901, 36, 290—304).—The velocity of hydrolysis of ethyl acetate by sodium hydroxide solutions was determined at temperatures of about 10° and 40°. The results for the velocity constant were 10°, 2.24; 39.33°, 13.17; 41.81°, 16.32. From these values, the constant in the Arrhenius formula for the temperature variation is calculated as (1) 5339, (2) 5562, numbers agreeing well with previous determinations. The hydrolysis was also effected by solutions of potassium cyanide, and from the results the hydrolytic decomposition of the latter was calculated; the values obtained are slightly higher than those found by Shields (*Abstr.*, 1893, ii, 448). The sodium salts of sucrose, dextrose, and lævulose were also investigated, and the values of the velocity constants obtained were compared with those found for potassium hydroxide; in all cases, the ratio increases with rise of temperature, and from the ratios the dissociation constant of the sodium compound was obtained. From the temperature coefficients, the heats of formation of the compounds are deduced. The value so obtained for potassium cyanide is 3424 cal., a value consider-

ably higher than that obtained directly. The values for the sodium compounds of the sugars are also far higher than would be expected, varying from 3302 to 6871. L. M. J.

Relations between Constitution and Reactive Power. By RUDOLF WEGSCHEIDER (*Chem. Centr.*, 1901, i, 356; from *Oesterr. Chem. Zeit.*, 4, 1—7).—The author discusses a law of conservation of linkings, according to which the number of linkings dissolved in any reaction is a minimum. Thus, in the addition of bromine to ethylene, it is probably the compound $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br}$ that is formed, because the formation of $\text{CHBr}_2\cdot\text{CH}_2$ would involve the dissolution of a larger number of linkings. The law is in so far subject to exception, as intermolecular changes are possible. The reactive power of a substance is its ability to undergo intermolecular changes with moderate velocity. This velocity depends on the nature of the atoms immediately concerned in the change of distribution of linkings, and also on the constitution of the molecule as a whole. The author points out several types of constitutional influence, although no reaction can be regarded as exemplifying one type alone. J. C. P.

Determination of the Avidity of Phenol by the Thermochemical Method. By I. S. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 51—61).—Using Thomsen's thermochemical method of measuring the heat developed when sodium hydroxide is neutralised by phenol and sulphuric acid together in solution, the author finds the avidity of phenol to have the value 0.0126, which is somewhat greater than that of boric acid. T. H. P.

Fractional Esterification and Hydrolysis of Stereoisomerides. By WILLY MARKWALD and ALEXANDER MCKENZIE (*Ber.*, 1901, 34, 469—478. Compare *Abstr.*, 1899, ii, 733).—The ratio of the velocities of esterification of *l*- and *d*-mandelic acids with *l*-menthol, calculated by the aid of the formula $c = \log \frac{a-x}{a} / \log \frac{b-y}{b}$ from the data previously given is 0.897. The ratio for the velocities of hydrolysis of the menthyl esters of the *l*- and *d*-acids is 0.910.

Although the *d*-acid is esterified somewhat more quickly than the *l*-acid, yet when the resulting ester obtained from *r*-mandelic acid is hydrolysed, the acid has a slight levorotation. This is now shown to be due to partial racemisation during esterification. Experiments made with phenylethoxyacetic acid (*Trans.*, 1899, 75, 758) have given similar results, but experiments with α -ethoxypropionic acid (*ibid.*, 487) indicate that no racemisation occurs during esterification with *l*-menthol.

The authors find that methyl-*n*-hexylcarbinol obtained from ricinoleic acid has a slight levorotation $\alpha_D - 10'$ ($l=2$), and that it is in reality a mixture of the *d*-*l*- and *l*-alcohols. When heated at 155° with two-thirds of its weight of *d*-tartaric acid, the *l*-alcohol is somewhat more quickly esterified than the *d*-alcohol; the difference, however, is but slight. When the resulting ester is hydrolysed, the ester of the *l*-alcohol is much more readily decomposed than that of the *d*-alcohol.

It is probable that the alcohol obtained from ricinoleic acid contains a certain amount of heptyl alcohol. J. J. S.

Eutectic Curves in Systems of Three Substances of which Two are Optical Antipodes. By J. H. ADRIANI (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 463—467).—It has been shown that the examination of the freezing point curve of solutions of active compounds furnishes a means of deciding whether an externally compensated inactive substance is a conglomerate, a racemic compound, or a pseudo-racemic mixed crystal. By the use of different solvents of high melting point, it may be further possible to find whether above a certain temperature the racemic compound decomposes into mixed crystals. Experiments with camphoroxime in naphthalene, phenanthrene, and benzoïn solutions showed that although a racemic compound exists at the temperature of 97°, yet in anthracene solution at 105·6° the *i*-oxime must be regarded as a mixed crystal of the active compounds, a result in accord with the author's previous investigations (*Abstr.*, 1900, ii, 462; *Bruni, Abstr.*, 1899, ii, 732).

L. M. J.

Two Cases of Catalysis in Non-homogeneous Systems. By KARL DRUCKER (*Zeit. physikal. Chem.*, 1901, 36, 173—215).—I. Anhydrous chromic chloride, obtained by sublimation, is practically insoluble in water, but in presence of reducing agents solution takes place, due to the transformation into the soluble modification.

The author has determined the amount of chromic chloride passing into solution in different times in presence of reducing agents, the reduction-potentials of which are measured in a capillary electrometer. Experiments have been made with Peters' ferrosiferic mixture, with and without addition of potassium fluoride (*Abstr.*, 1898, ii, 419), ferrous sulphate and sulphuric acid, ferrous oxalate, hydroxylamine sulphate, cuprous chloride, mercurous chloride, and a few other reducing agents. The calculated rates of solution do not give an entirely satisfactory constant value, but the results show that the rate is dependent upon (1) the nature of the reducing agent, (2) its reduction-potential, increasing and decreasing with this, and (3) its absolute concentration. In presence of a sparingly soluble reducing agent, solution of the chromic chloride only takes place provided that the agent is also present in the solid state. The author believes that the function of the reducing agent is not entirely catalytic, but that reaction takes place between this and the chromic chloride. Solution is probably preceded by a slight reduction to chromous chloride, the catalytic influence of which is very great; only a small quantity of this can, however, be formed, since its potential in solutions of appreciable concentration is greater than that of hydrogen, whilst the potential in the solution cannot rise above that of the reducing agent present. It has not been proved that the catalytic influence is wholly due to chromous chloride. Loewel's hypothesis (*J. Pharm.*, 1843, [iii], 4, 424) is discussed and shown to be insufficient, as also is Recoura's interpretation of it (*Abstr.*, 1886, 669).

II. The rate of solution of arsenious oxide in presence of sulphuric acid, acetic acid, oxalic acid, some alkali salts, ethyl or amyl alcohols,

or mannitol has been determined. A constant value, in agreement with the researches of Noyes and Whitney (Abstr., 1897, ii, 479), has been obtained in each set of experiments for the rate of solution. Amyl alcohol slightly decreases the rate, but all the other substances increase it. Hydrogen ions exert a strong catalytic action—sulphuric acid having a much greater influence than acetic acid on account of the greater degree of dissociation. The hydroxyl ion is a stronger catalyser than the hydrogen ion. The solubility of arsenious oxide in these various solvents is not appreciably different from that in pure water. J. McC.

The Standard of Atomic Weights. By BOHUSLAV BRAUNER (*Zeit. anorg. Chem.*, 1901, 26, 186—202).—A reply to certain objections to the standard $O = 16$, which have been raised from the pedagogic standpoint. T. E.

So-called Liquid Crystals. By GUSTAV TAMMANN (*Ann. Phys.*, 1901, [iv], 4, 524—530. Compare Schenck, Abstr., 1898, ii, 286, 563; 1899, ii, 360; Schenck and Schneider, Abstr., 1899, ii, 637; Abegg and Seitz, Abstr., 1899, ii, 623).—It is possible to regard the turbid liquids obtained on melting clear crystals of *p*-azoxyanisole or *p*-azoxyphenetole as emulsions of a brown reduction product in the fused compounds; the clear crystals may be regarded as solutions of the brown reduction product in the crystals of these compounds. The author holds that so-called crystalline liquids have not been definitely proved to exhibit characteristic double refraction. The temperature at which turbidity disappears is lowered by the addition of other substances (Schenck and Schneider, *loc. cit.*), a phenomenon which may be attributed simply to an increased solubility of the reduction product in presence of other substances. If the so-called liquid crystals are really mechanical mixtures of two liquids, it must be possible to separate them, to raise the melting point of the solid crystals, and to lower the temperature at which turbidity disappears. By repeated distillation in a current of superheated steam, the temperature at which turbidity disappears in the case of *p*-azoxyanisole was lowered 6.5° ; the experiments, however, are not yet completed. Cholesteryl benzoate, which Lehmann regards as giving a crystalline liquid on melting, is unsuited for investigation because of its doubtful chemical homogeneity. J. C. P.

Physical Properties of Albuminous Micelles. By SWIGEL POSTERNAK (*Ann. Inst. Pasteur*, 1901, 15, 85—120).—A "micelle" is used to denote the smallest quantity of a colloid which possesses all the physical properties of the colloid and is formed by the association of molecules of large size. The paper does not lend itself to abstraction. The precipitation of colloidal substances by solutions of chemical reagents depends on the concentration of the ions of the latter. R. H. P.

Devices for Circulating Liquids at Constant Temperature. By IRA H. DERBY (*J. Physical Chem.*, 1901, 5, 17—20).—The apparatus described is stated to realise the following conditions. Rapidity of circulation, ease of construction, economy, rapidity of

adjustment, constancy of temperature, great range of temperature. Into a large thermostat the ends of the circulating tubes dip, and are filled by suction. The reflux tube is encircled by a loosely fitting tube ending in a bulb, in which two side holes of about 1 cm. diameter are blown. This tube is rapidly rotated by a suitable motor, and in consequence of the centrifugal force, the water is driven out through the side holes and drawn through the tubes, whilst further, this scattering of the return water through the bath obviates the necessity for an independent stirrer.

L. M. J.

Inorganic Chemistry.

Inorganic Chemistry and Physical Chemistry. By CLEMENS WINKLER (*Ber.*, 1901, 34, 393—399).—A plea for the more efficient study of inorganic chemistry as distinct from physical chemistry, particularly with reference to its employment in the development of the new electrochemical industries.
G. T. M.

Combustible Gases of the Atmosphere : Atmospheric Hydrogen. By ARMAND GAUTIER (*Ann. Chim. Phys.*, 1901, [iii], 22, 5—110).—A detailed account of work already published, containing also a discussion as to the origin of atmospheric hydrogen not suitable for abstraction (compare *Abstr.*, 1898, ii, 535, 537, 640, 641 ; 1899, ii, 149 ; 1900, ii, 469, 537, 538, 720 ; and this vol., ii, 14, 92, and 171).
G. T. M.

Explosion of Mixtures of Combustible Vapours or Fumes and Air. By K. KUBIERSCHKY (*Zeit. angew. Chem.*, 1901, 14, 129—132).—The following percentages show the least amount of vapour which will explode with 100 volumes of air: benzene, 1.4 ; toluene, 1.4 ; ethyl alcohol, 4.0 ; methyl alcohol, 7.8 ; acetone, 2.7 ; ethyl ether, 1.8 ; carbon disulphide, 4.1. The gases resulting from the combustion of alcohol have a higher specific heat than those from benzene and similar hydrocarbons, so that the latter are better for use with explosion motors. Carbon disulphide readily explodes with air ; when the carbon disulphide is in excess, sulphur separates, and when the air is in excess, sulphur trioxide is formed. A mixture of 2 parts of benzene with 3 parts of carbon tetrachloride will not explode with air, but burns quietly with a very luminous flame. For the preparation of these explosive mixtures, it is not necessary that the combustible substance should be vaporised, since air, in which the combustible substance is suspended as a mist or fumes, behaves in the same manner as a mixture of air and the vaporised substance.

R. H. P.

Method for Determining the Molecular Weight of Ozone. By ALBERT LADENBURG (*Ber.*, 1901, 34, 631—635).—The molecular

weight of ozone was determined by weighing a bulb first when filled with oxygen, and then when filled with a quantity of the same sample of oxygen ozonised to the extent of 4 to 8 per cent.; the increase in weight gave the weight of active oxygen, and the total volume of ozone was determined by absorption with turpentine. The mean of five determinations of the molecular weight was 47.78, the extreme values being 45.3 and 50.4.

T. M. L.

Sulphuryl Fluoride. A New Gas. By HENRI MOISSAN and PIERRE LEBEAU (*Compt. rend.*, 1901, 132, 374—381. Compare Abstr., 1900, ii, 341, 472).—*Sulphuryl fluoride*, SO_2F_2 , is prepared by passing fluorine into an apparatus containing sulphur dioxide so disposed that the former gas as it reaches the latter is strongly heated by means of a platinum wire placed at the inner end of the inlet tube and rendered incandescent by an electric current. Without this device, the combination of the gases is delayed, and then subsequently takes place with explosive violence. The new gas may also be obtained by passing fluorine into moist hydrogen sulphide, when the former burns quietly with a blue flame; the product also contains silicon fluoride, sulphur hexafluoride, and thionyl fluoride; when the experiment is performed in glass vessels, the presence of moisture is not essential, the necessary oxygen being derived from the action of the hydrogen fluoride produced on the silica. The sulphuryl fluoride, freed from the other products by washing with water and with copper sulphate solution, is dried over fused potassium fluoride, liquefied, and fractionated in a vacuum.

The compound is a colourless, odourless gas boiling at -52° and melting at -120° , its vapour pressures at -120° and -80° being 65 and 241 mm. respectively. It is stable at temperatures below a dull red heat, but when strongly heated in glass vessels it interacts with the silica, yielding silicon fluoride, sulphur trioxide, and small quantities of sulphur dioxide. Sulphuryl fluoride is insoluble in concentrated sulphuric acid, but 1 part of the gas dissolves in 10 parts of water at 9° , whilst alcohol absorbs three times its volume of the compound at the same temperature; it is slowly absorbed by aqueous solutions of potassium, calcium, or barium hydroxides, and is rapidly dissolved by alcoholic solutions of the alkali hydroxides. Fluorine is without action on the gas even at 200° , and oxygen produces but a slight decomposition even by the aid of the electric spark; hydrogen at red heat furnishes a white, solid substance yielding sulphuric and hydrofluoric acids on treatment with water. Sulphur and selenium readily decompose the gas at a red heat with the formation of silicon fluoride and their respective lower oxides; phosphorus, arsenic, carbon, and boron, on the other hand, have no action on the compound; silicon produces a slight decomposition, but the reaction is not complete even after 1 hour.

Iron and magnesium do not interact with the gas even at a red heat, sodium and calcium, however, completely absorb it, forming the corresponding sulphides and fluorides, the reaction with sodium being employed in the analysis of the compound.

A mixture of hydrogen sulphide and the new fluoride, when heated

to a dull red heat, yields a deposit of sulphur, but no change occurs when the fluoride is heated with hydrogen chloride.

A white solid compound, $\text{SO}_2\text{F}_2 \cdot 5\text{NH}_3$, soluble in water, is produced by the direct union of its generators at the ordinary temperature.

G. T. M.

Preparation and Properties of Sulphammonium. By HENRI MOISSAN (*Compt. rend.*, 1901, 132, 510—518. Compare Abstr., 1899, ii, 152).—The octahedral, prismatic, and insoluble modifications of sulphur are not affected by dry liquid ammonia at -80° , but dissolve yielding purple solutions when the temperature rises to -38° , -15.5° , and -11.5° respectively. The solutions thus obtained seem to contain the sulphur in a state of combination, for they solidify at temperatures 4° or 5° below the melting point of solid ammonia without depositing any of the element. Moreover, quantitative experiments indicate that sulphur is quite insoluble in liquid ammonia at temperatures below that at which the purple coloration is developed. The name *sulphammonium* is given to the substance whose existence is thus indicated; the product, however, appears to vary considerably in composition, at -28° corresponding with the formula $\text{S}(\text{NH}_3)_2 \cdot 2\text{NH}_3$, and at 0 — 20° with $\text{S}(\text{NH}_3)_2 \cdot \text{NH}_3$. Sulphammonium is stable at comparatively high temperatures, its solution, when heated in sealed tubes from -11.5° to 90° , being intensely coloured; at higher temperatures, however, the colour fades, and entirely disappears at 131° , the critical temperature of ammonia. The globules of melted sulphur now noticed on the sides of the tubes remain undissolved until the temperature of the ammonia falls to 100° ; at this point, the coloration reappears and increases in intensity as the temperature falls.

In sealed tubes at 20° , the sulphammonium is partially dissociated, equilibrium being attained when the solution contains 30 per cent. of sulphur; when the pressure is released, the soluble product is completely decomposed with the deposition of sulphur. The coloration developed by adding sulphur to liquid ammonia maintained at -35° under the ordinary pressure is very faint, the dissociation of the sulphammonium, under these conditions, being almost complete. In sealed tubes, on the other hand, the amount of sulphur dissolved in a given quantity of ammonia increases as the temperature diminishes, and well-defined sulphur crystals may be produced by slowly raising to 20° the temperature of solutions prepared at -40° .

Red, fern-like leaflets of the solid sulphammonium are produced by submitting a mixture of nitrogen and ammonia at -12° to a pressure of 45 atmospheres in the presence of sulphur. Sulphammonium has a very characteristic absorption spectrum, this property serving as a means of detecting small quantities of sulphur. An ammonia solution containing 0.0061 per cent. of sulphur has a distinctly red colour, and gives an absorption spectrum containing two bands, one cutting off the orange and yellow parts of the spectrum, the other the whole of the blue rays with portions of the green and violet. A more concentrated solution cuts off all the light except a green band and the least refrangible portion of the red end of the spectrum. Sulphammonium dissolves in absolute alcohol and ether, in the latter case yielding at

-80° a purple solution turning blue on dilution; at -40° , however, the product is decomposed, with liberation of sulphur. Liquids miscible with ammonia lower its vapour pressure, and consequently increase the dissociation of sulphammonium; this substance yields, with benzene and carbon disulphide, brown and blue solutions respectively, whilst carbon tetrachloride yields colourless crystals and an orange compound dissociating under the ordinary pressure. Sulphammonium interacts with many substances, yielding sulphur derivatives; with iodine, it furnishes a compound of ammonia and sulphur iodide, and with calcium-ammonia either white calcium monosulphide or the corresponding red persulphide, depending on the proportions of the reagents. Mercuric, lead, and manganese chlorides and the oxides of zinc and calcium interact with sulphammonium, giving rise to unstable products; mercury also is attacked, with the formation of the black sulphide, whilst selenium and the alkali haloid salts are not affected. G. T. M.

Replacements in the Sulphur-Selenium-Tellurium Group. By FRIEDRICH KRAFFT and O. STEINER (*Ber.*, 1901, **34**, 560—565).—When phenyl selenide, SePh_2 , is heated nearly to the boiling point with sulphur, diphenyl sulphide is produced and selenium liberated, the reaction being practically quantitative at 300° . Phenyl telluride undergoes a similar change when heated with sulphur, tellurium and phenyl sulphide being formed. Phenyl sulphide, on the other hand, is not affected by oxygen, whilst phenyl ether, when heated at 550° with sulphur, yields phenyl sulphide. It seems probable that in all these cases additive compounds are first formed. In the last case, this product would be phenyl sulphoxide, SOPh_2 , and this substance itself decomposes slowly at 340° into phenyl sulphide and oxygen (Krafft and Lyons, *Abstr.*, 1896, i, 297). In the same way, the preparation of phenyl sulphide and selenide from sulphobenzide, SO_2Ph_2 , by heating with sulphur or selenium, probably depends on the formation of an intermediate additive compound. Oxy-phenyldisulphide, $\text{SO}_2\cdot\text{SPh}_2$, which would be formed by sulphur is known (Otto, *Annalen*, 1868, **145**, 318), and this, when heated, actually yields sulphur dioxide and phenyl sulphide.

Selenious oxide is readily decomposed by sulphur at the temperature of melting sulphur. This replacement can be carried out as a lecture experiment in an atmosphere of carbon dioxide in a sealed tube. After cooling, the tube is found to contain black selenium and liquid sulphur dioxide.

Selenic acid is converted by sulphur at 55° into selenious acid, sulphuric acid being produced at the same time. Whilst the affinity for oxygen appears to decrease as the atomic weight rises in this group, that for chlorine increases, tellurium tetrachloride being the most stable, and sulphur tetrachloride the most easily decomposed. Corresponding with this, it is found that sulphur dichloride is decomposed both by selenium and tellurium, free sulphur being formed in both cases, together with a chloride of the element employed. A. H.

Replacements in the Phosphorus-Arsenic-Antimony Group. By FRIEDRICH KRAFFT and R. NEUMANN (*Ber.*, 1901, **34**, 565—569).—In the phosphorus group, it is found that arsenic replaces phosphorus,

and antimony both arsenic and phosphorus in the oxides, sulphides, and chlorides, whilst the order of replacement is the reverse of this with the triphenyl compounds. Phosphorous oxide is quantitatively decomposed by an excess of arsenic at 290° , arsenious oxide and phosphorus being produced, whilst both phosphorous and arsenious oxides are decomposed in a similar manner by antimony. In the same way, phosphorus trisulphide is decomposed by arsenic and by antimony, and arsenic trisulphide by antimony, at temperatures above 300° , more than 90 per cent. of the theoretical amount of product being in each case obtained. Phosphorus trichloride is scarcely affected by arsenic, but when a little arsenic chloride is added, the reaction proceeds almost quantitatively at 200° . The decomposition of phosphorus trichloride by antimony has previously been observed (Baudrimont, *Ann. Chim. Phys.*, 1864, [iv], 2, 5), and arsenic chloride undergoes a similar decomposition at 200° . On the other hand, triphenylarsine is quantitatively decomposed by phosphorus at 300° , whilst triphenylstibine is similarly decomposed by arsenic at 350° .

A. H.

Phenyl Telluride and the Atomic Weight of Tellurium. By O. STEINER (*Ber.*, 1901, 34, 570—572).—Phenyl telluride is readily volatile, and can be prepared pure and free from admixture with other compounds. The author has therefore very carefully estimated the carbon and hydrogen in this compound by combustion in presence of lead chromate, and from these results calculated the atomic weight of tellurium. The mean of five determinations gives the number 126.4 (oxygen = 16), which is distinctly less than the atomic weight of iodine, 126.85. An error of 0.1 per cent. in the carbon affects the atomic weight of tellurium by 0.5, and the separate numbers obtained vary from 126.1 to 126.7. The result is only regarded as a preliminary one to be confirmed by a direct estimation of the tellurium.

A. H.

Detection of Nitrogen in Arsenic, and the Conversion of Arsenic into Antimony. By FRIEDRICH FITTICA (*Chem. Zeit.*, 1901, 25, 41. Compare Christomanos, this vol., ii, 59).—Nitrogen in arsenic may readily be detected by conversion into boron nitride; the boron and arsenic are heated at 250 — 300° , and then extracted first with nitric, and then with hydrochloric acid, when the nitride remains undissolved; the solution, in addition to arsenic acid, contains a considerable amount of antimony chloride. In the author's opinion, the arsenic is resolved into nitrogen and antimony (compare this vol., ii, 59).

J. J. S.

Detection of Nitrogen in Arsenic, &c. By CARL ARNOLD and F. MURACH (*Chem. Zeit.*, 1901, 25, 131).—Fittica (preceding abstract) has stated that arsenic when heated with boron yields, not only antimony, but also boron nitride, and consequently contains nitrogen. The authors have repeated the experiments, using pure boron, prepared by igniting anhydrous borax with magnesium powder in a current of hydrogen. Not a trace of hydrogen or antimony could be obtained from pure arsenic.

L. DE K.

Behaviour of Arsenious Oxide towards Permanganate. By OTTO KUEHLING (*Ber.*, 1901, **34**, 404—406. Compare this vol., ii, 38).—When slightly alkaline solutions of arsenious oxide containing zinc sulphate are titrated with standard potassium permanganate solution, the colour rapidly disappears in the cold until 70—80 per cent. of the oxide is oxidised; beyond this point the coloration persists, and is destroyed only on prolonged heating of the solution at the temperature of the water-bath.

Arsenious oxide, when dissolved in boiling 30—40 per cent. sulphuric acid, is rapidly oxidised by the permanganate without the employment of zinc sulphate; towards the close of the titration, the solution requires to be heated for 1—2 minutes after each addition of oxidising agent.

G. T. M.

Action of Hydrogen Sulphide on Boron Bromide. By ALFRED STOCK and OTTO POPPENBERG (*Ber.*, 1901, **34**, 399—403).—*Metathioboric acid*, B_2S_3, H_2S , prepared by saturating a hot solution of boron bromide in carbon disulphide or benzene with dry hydrogen sulphide, crystallises from these solvents in long, white needles having an odour of hydrogen sulphide; this gas is evolved when the crystals are heated at 100° , and on raising the temperature to 300° pure boron sulphide remains. The molecular weight, as determined by the cryoscopic method in benzene, corresponds with that required by the above formula. During the preparation of the thio-acid, the tube conveying the hydrogen sulphide into the boron bromide solution rapidly becomes choked with crystals of the product, and the paper includes a description and sketch of an apparatus devised to overcome this difficulty. The thio-acid is energetically decomposed by water with the formation of hydrogen sulphide and boric acid; it undergoes a similar decomposition with alcohol, and appears to combine with ether; it differs markedly from the trisulphide in its solubility in benzene and carbon disulphide, one part dissolving in five parts of either of these solvents.

Hydrogen sulphide has no action on boron chloride below a dull red heat, and even then the reaction is only incomplete, the product being a mixture of boron sulphide and unaltered chloride.

G. T. M.

Argon and its Companions. By WILLIAM RAMSAY and MORRIS W. TRAVERS (*Proc. Roy. Soc.*, 1901, **67**, 329—333. Compare *Abstr.*, 1898, ii, 574; 1899, ii, 211).—The phosphorus previously used to remove oxygen from the mixture of atmospheric gases has been found to contain carbon, and the spectrum formerly attributed to a new element metargon is now referred to some carbon compound.

When a large amount of liquid air is allowed to evaporate quietly, the residue, after removal of the oxygen and nitrogen, consists of krypton, xenon, and argon, the last-mentioned being the main constituent. Argon is the most volatile of the three, and the separate gases may be obtained by alternate liquefaction and evaporation. At the temperature of boiling air, krypton has a considerable vapour pressure, whilst that of xenon is hardly appreciable.

To obtain neon and helium, the gas escaping from an air liquefier is used; this gas (consisting largely of nitrogen) is liquefied, and a

current of air is blown through the liquid; the first portion of the liquid to evaporate contains most of the neon and helium present in the air, along with oxygen, nitrogen, and argon. The oxygen and nitrogen are removed in the usual manner, and fractional distillation separates the neon and helium from the argon. Neon may be obtained free from helium by a few fractionations at the temperature of boiling hydrogen; neon is liquefied or perhaps solidified at this temperature, whilst helium remains in the gaseous state.

The five gases, helium, neon, argon, krypton, and xenon are all monoatomic, for the ratio of the specific heats, as determined by Kundt's method, is 1.66 in each case. Other physical constants are given below:

| | Argon. | Krypton. | Xenon. |
|---------------------------------------|--------|----------|--------|
| Refractivity (air = 1) | 0.968 | 1.449 | 2.364 |
| Density (O = 16) | 19.96 | 40.88 | 64 |
| Boiling point (abs. at 760 mm.) | 86.9° | 121.33° | 163.9° |
| Critical temperature (abs.) | 155.6° | 210.5° | 287.7° |
| Critical pressure (metres) | 40.2 | 41.24 | 43.5 |
| Vapour pressure ratio | 0.0350 | 0.0467 | 0.0675 |
| Weight (grams) of 1 cub. cm. liquid | 1.212 | 2.155 | 3.52 |
| Molecular volume..... | 32.92 | 37.84 | 36.40 |

The refractivities of helium and neon are 0.1238 and 0.2345, their densities are 1.98 and 9.97 respectively; the critical temperature of neon is below 68° abs.

The compressibilities of the gases were measured at 11.2° and 237.3°. At 11.2°, as is known, the product pv for hydrogen increases with rise of pressure, whilst for nitrogen it first decreases and then increases. With helium, the increase is more rapid than with hydrogen; with argon, there is first a considerable decrease followed at very high pressures by a gentle increase, although the product does not reach the theoretical value at 100 atmospheres pressure; with krypton, the change with rise of pressure is a still more marked decrease, and with xenon the decrease is very sudden. At the higher temperature, the results are more difficult to interpret.

The spectra of the gases have been measured by E. C. C. Baly. The colour of a neon tube is extremely brilliant and of an orange-pink hue; that of krypton is pale violet, and that of xenon is sky-blue.

The authors hold that the gases form a series in the periodic table (He = 4, Ne = 20, A = 40, Kr = 82, X = 128) between that of fluorine and that of sodium. They exhibit gradations in properties such as refractive index, atomic volume, melting point and boiling point, and the specific heat ratio has the same value for each gas. If the densities be regarded as identical with the atomic weights, as in the case of diatomic gases like hydrogen and oxygen, there is no place for the new elements in the periodic table. J. C. P.

Some Conditions of Reversibility. By ALBERT COLSON (*Compt. rend.*, 1901, 132, 467—469).—When dry silver carbonate is heated in a bsence of water vapour, there is a definite dissociation pressure

for a given temperature, whatever the mass of the silver carbonate, but the reaction is not reversible. In presence of a small quantity of water vapour, however, it is reversible.

Carbon monoxide reduces silver oxide energetically at 10° , but at -21° there is very little reduction, although sometimes the gas is absorbed or is replaced by an equal volume of carbon dioxide, silver carbonate being formed.

Red mercuric oxide has no action on carbon monoxide in the dark at the ordinary temperature, but the yellow oxide rapidly converts it into carbon dioxide. In the light, the red oxide blackens slowly in contact with carbon monoxide, and carbon dioxide is formed, whilst the yellow oxide rapidly absorbs carbon monoxide, causing a reduction of pressure simultaneously with the formation of carbon dioxide.

C. H. B.

Action of Acids on Carbonates of the Alkaline Earth Metals in Presence of Alcohol. By C. VALLÉE (*Compt. rend.*, 1901, 132, 677—678).—Calcium carbonate, when suspended in absolute alcohol, was decomposed with extreme slowness by sulphuric or acetic acid, the time required for the complete neutralisation of the acid being 4 months in the former case and $3\frac{1}{2}$ in the latter; similar results were obtained with nitric acid. Analogous experiments were made with strontium and barium carbonates, and it was found that the velocity of reaction in the case of the latter compound was much less than in that of the calcium salt. On employing dilute alcohol as the medium, the velocity of neutralisation is greatly increased, the rate of change diminishing with the time, and being proportional to the amount of water present; the reaction is not notably affected by temperature.

G. T. M.

Atomic Weight of Calcium. By ALEXANDER HERZFELD [and CARL STIEPEL] (*Ber.*, 1901, 34, 559—560).—The atomic weight of calcium obtained as a mean of three analyses of calcium carbonate, prepared from a solution of calcium hydrogen carbonate, is 39.673 (hydrogen = 1) or 39.962 (oxygen = 16).

A. H.

Formation and Composition of Bleaching Powder. By HUGO DITZ (*Zeit. angew. Chem.*, 1901, 14, 3—14, 25—31, 49—57, and 105—111).—According to the author, at low temperatures, 2 mols. of calcium hydroxide react with 1 mol. of chlorine, yielding the compound $\text{CaO}, \text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O}$, which, if the temperature is not kept very low, undergoes dissociation under the influence of water into calcium hydroxide and the compound $\text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O}$; the hydroxide then reacts with more chlorine, yielding the compound $2\text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O} + \text{CaO}, \text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O} + \text{H}_2\text{O}$ or $6\text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O} + \text{CaO}, \text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O} + \text{H}_2\text{O}$. With an increase in the amount of water present, it is possible to obtain bleaching powders of higher percentage, until finally a product containing only 0.61 per cent. of unchlorinated calcium oxide, in the form of $\text{CaO}, \text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O}$, results.

The reactions may be written generally, $2n\text{Ca}(\text{OH})_2 + (2n-1)\text{CaCl}_2 = (2n-2)\text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O} + \text{CaO}, \text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O} + \text{H}_2\text{O}$.

The compound $\text{CaO}, \text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O}$ does not lose its water at 100° ;

at higher temperatures, oxygen is evolved and the compound $\text{CaO}, \text{CaCl}_2, \text{H}_2\text{O}$ left behind.

The compound $\text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O}$, which probably has the double molecular formula, evolves chlorine and water when heated at 100° in an atmosphere of dry carbon dioxide, leaving the compound $\text{CaO}, \text{CaCl} \cdot \text{OCl}, \text{H}_2\text{O}$.
J. J. S.

Formation of Magnesium Nitride by Heating Magnesium in Air. By WILHELM EIDMANN and L. MOESER (*Ber.*, 1901, **34**, 390—393).—Magnesium nitride can be prepared by heating in air magnesium powder mixed with a number of oxides of metals which readily oxidise, and also by heating with certain metals and carbides. A mixture of equal parts of iron and magnesium, heated in an uncovered crucible, gave a crude product containing 36 per cent. of the nitride.

By heating magnesium powder strongly in a covered crucible with a minute opening in the cover, a lower layer of nitride is formed, covered with unchanged magnesium, and a surface layer of oxide. By carefully regulating the conditions, as much as 78—80 per cent. of nitride can be obtained in the product, a value approaching very nearly to that required for a complete absorption of the oxygen and nitrogen of the air (calc. 82.3 per cent.).
T. M. L.

Action of Substituted Ammonia Bases on Zinc Salts, and a New Method for the Estimation of Zinc. By W. HERZ (*Zeit. anorg. Chem.*, 1901, **26**, 90—93).—When a solution of zinc sulphate is treated with methylamine or dimethylamine, a quantitative reaction takes place and zinc hydroxide and the sulphate of the base are formed. In the case of methylamine, an excess of this compound forms complex compounds with the precipitated zinc hydroxide, but these complex compounds are not formed with dimethylamine.

Zinc can be estimated accurately by precipitating the zinc salt with excess of dimethylamine, the precipitate of zinc hydroxide being then treated in the usual manner.
E. C. R.

Alkali-Copper Carbonates. By MAX GRÖGER (*Ber.*, 1901, **34**, 429—432).—The silky, greenish-blue needles, which slowly form from a mixture of potassium hydrogen carbonate and copper sulphate solutions, probably have the composition $8\text{CuO}, 2\text{K}_2\text{CO}_3, 7\text{CO}_2, 17\text{H}_2\text{O}$. Sodium copper carbonate, $\text{Na}_2\text{CO}_3, \text{CuCO}_3, 3\text{H}_2\text{O}$, separates in the form of clusters of bright blue crystals, when a mixture is made of solutions of sodium, sodium hydrogen carbonate, and copper carbonate.

R. H. P.

Nature of Lead Amalgams. By HENRY FAX and EDWARD NORTH (*Amer. Chem. J.*, 1901, **25**, 216—231).—Amalgams of lead were prepared of varying composition, and their rate of heating or cooling examined by means of a platinum-rhodium thermoelectric couple immersed in them, a marked decrease in the rate indicating the melting point. As the percentage of lead increases, the melting point remains practically constant; it is slightly above that of pure mercury, -39.4° . These amalgams are not entirely liquid; they grow

more and more pasty as the percentage of lead increases. By centrifugalising them in a chamois bag, crystals are obtained of the composition Pb_2Hg (compare Joule, this Journ., 1863, 16, 378). When the percentage of lead has reached 65, the amalgam is entirely solid; the melting point is 177° , and now increases proportionally to the increase in the lead until the melting point of pure lead is reached. These facts suggest that lead and mercury form a compound, Pb_2Hg , which is isomorphous with lead, and miscible with it, but only slightly soluble in mercury. The micro-structure of the solid amalgams confirms this idea of isomorphism; no separation into constituents is visible when these amalgams are etched.

C. F. B.

Behaviour of Lead Salts in Solution. By CARL L. VON ENDE (*Zeit. anorg. Chem.*, 1901, 26, 129—166).—The solubility of lead chloride in water containing hydrochloric acid and potassium chloride is determined. At 25.2° , the saturated solution of lead chloride in pure water contains 0.0388 gram-mol. per litre, the addition of hydrochloric acid diminishes the solubility, a minimum solubility of 0.00441 gram-mol. per litre being attained in 1.026*N* hydrochloric acid; the solubility then increases, becoming 0.1643 gram-mol. per litre in 12.05*N* acid. Similar results are obtained with potassium chloride, the minimum solubility, 0.00483 gram-mol. per litre (at 25.2°), being reached in 1.5018 *N* potassium chloride solution.

The application of the theory of the solubility of mixed electrolytes containing a common ion to the above results leads the author (certain plausible assumptions being made) to the conclusion that the aqueous solution of lead chloride is dissociated partly into PbCl^+ , partly into Pb^{++} ions. In the saturated solution, 6.2 per cent. of the salt is undissociated, 50.1 per cent. is dissociated into Pb^{++} and $2\text{Cl}'$ ions, and 43.7 per cent. into PbCl^+ and Cl' ions. Practically none of it is hydrolysed.

The solubility of lead bromide in water at 25.2° is 0.02628 gram-mol., and that of lead iodide 0.00158 gram-mol. per litre.

All three lead salts are more soluble in presence of nitric acid or potassium nitrate, which is explained by the formation of PbNO_3^+ ions; this diminishes the number of Pb^{++} ions in solution and so causes dissociation of a further quantity of lead chloride which is replaced by the dissolution of the solid salt.

T. E.

Dissolution of Solid Metals in Mercury, and more generally in other Fused Metals. By M. BERTHELOT (*Compt. rend.*, 1901, 132, 290—291).—The liquids obtained by the dissolution of metals in mercury and fused metals are to be compared with emulsions rather than with ordinary solutions, and the spontaneous solidification of certain amalgams used in dentistry may be regarded as analogous to coagulation. The softening and disintegrating action of mercury on metals resembles the action of water on colloidal substances, either organic or inorganic. The results of the author's previous experiments on the heats of transformation of allotropic modifications of silver and on the heats of formation of silver amalgams are independent

of our ideas as to the nature of metallic solutions, since, in the experiments referred to, the final states were identical in all cases and the heat developed therefore truly represented the differences in the energy of the initial states. N. L.

Indium. By CAMILLE CHABRIÉ and ETIENNE RENGADE (*Compt. rend.*, 1901, 132, 472—475).—Dilute aqueous solutions of indium caesium alum, when boiled for a long time, yield a precipitate of indium oxide free from caesium or sulphuric acid; whilst indium rubidium alum is almost completely decomposed, and yields a precipitate of indium oxide containing also sulphuric acid and rubidium. The composition of indium rubidium alum agrees with that required by the ordinary formula; 100 parts of water dissolve 44.28 parts of the salt at 15°.

The boiling points of solutions of indium acetylacetonate in ethylene bromide show that the indium is trivalent; similar experiments with aluminium and iron acetylacetonates show that those metals are also trivalent under the same conditions. Combes' determination of the vapour density of aluminium acetylacetonate also showed that the aluminium was trivalent. It would seem clear therefore, that indium is analogous to iron and aluminium, and there is little reason to doubt that at the ordinary temperature the formula of its chloride is In_2Cl_6 . It is noteworthy, however, that indium readily forms an amalgam and in this respect resembles the metals of the zinc group.

C. H. B.

A New Cobalt Silicide. By PAUL LEBEAU (*Compt. rend.*, 1901, 132, 556—558. Compare *Abstr.*, 1899, ii, 427).—*Cobalt silicide*, CoSi , is produced in the form of prismatic needles by heating for 4—5 minutes in a carbon crucible placed in the electric furnace a mixture of copper silicide and metallic cobalt; when an electric current of 950 amperes and 50 volts is employed, the yield is 95 per cent. of the theoretical. The new compound melts at 1300° in a current of hydrogen, and has sp. gr. 6.30 at 20°.

Cobalt silicide is decomposed into fluorides with incandescence when gently heated in a current of fluorine; chlorine reacts only at a dull red heat; hydrogen fluoride or chloride decomposes the substance at high temperatures, yielding hydrogen and the corresponding haloid compounds of silicon and cobalt. Sulphur has no action on the compound at the fusing point of glass; oxygen, nitrogen, ammonia, and steam, under these conditions, decompose the silicide only superficially; hydrogen sulphide, at high temperatures, gives rise to sulphides of cobalt and silicon. Nitric and sulphuric acids do not attack the silicide; it dissolves, however, slowly in aqua regia, and more rapidly in hydrochloric acid.

Cobalt silicide is insoluble in dilute alkaline solutions, but is decomposed by the alkali hydroxides, either fused or in concentrated solutions. Fused potassium nitrate and potassium hydrogen sulphate have no action on the substance; melted potassium carbonate attacks it only slowly.

G. T. M.

Ammoniacal Arsenates of Cobalt and Nickel ; Application in the Estimation of Arsenic. By O. DUCRU (*Ann. Chim. Phys.*, 1901, [vii], 22, 160—238. Compare this vol., ii, 23, 73, 125).—A detailed account of work already published. G. T. M.

Action of Water on Molybdenum Pentachloride. By MARCEL GUICHARD (*Bull. Soc. Chim.*, 1901, [iii], 25, 188—191).—The liquid obtained by the action of water on molybdenum pentachloride exhibits all the characters of a solution of the tetrachloride, and quantitative experiments show that decomposition occurs according to the equation $2\text{MoCl}_5 + 3\text{H}_2\text{O} = \text{MoCl}_4 + \text{MoO}_3 + 6\text{HCl}$. When exposed to the air, the solution becomes blue, and then contains the oxide $\text{MoO}_3, 4\text{MoO}_3$. N. L.

New Crystallised Molybdenum Sulphate. By G. BAILHACHE (*Compt. rend.*, 1901, 132, 475—478).—When a rapid current of hydrogen sulphide is passed through a boiling solution of molybdenum trioxide in six times its weight of sulphuric acid, the compound $\text{Mo}_2\text{O}_5, 2\text{SO}_3$ is obtained as a mass of black, olive prisms, slowly but completely soluble in water, and yielding a deep brown solution if kept out of contact with air. When exposed to air, the compound deliquesces and its aqueous solution becomes green and then blue. The brown solution is readily oxidised to molybdic acid ; when mixed with an alkali molybdate, it yields the blue molybdenum oxide, and when mixed with an alkali it yields a soluble molybdate and a precipitate of hydrated molybdenum dioxide.

When heated alone, the compound yields molybdic, sulphuric, and sulphurous oxides ; hot sulphuric acid converts it into the compound $\text{MoO}_3, \text{SO}_3$; hydrogen at a red heat converts it into molybdenum dioxide and sulphuric acid, and dry ammonia also reduces it at a dull red heat. When heated with an intimate mixture of sodium chloride or bromide, it yields molybdenum oxychloride, MoO_2Cl_2 , or the oxybromide, together with molybdenum dioxide, sodium anhydrosulphate, and sodium anhydromolybdate, the proportions of the two latter depending on the duration of the operation. C. H. B.

Reduction of Molybdosulphuric Acid by Alcohol. By E. PÉCHARD (*Compt. rend.*, 1901, 132, 628—631).—When alcohol is gradually added to a solution of molybdic acid in sulphuric acid and the liquid warmed on the water-bath for a short time, diluted, and neutralised with ammonia, a crystalline precipitate is produced which consists of a mixture of two compounds, one, of the composition $5\text{NH}_3, \text{MoO}_2\text{SO}_3, 7\text{MoO}_3, 8\text{H}_2\text{O}$, crystallising in blue, hexagonal plates, and the other, $3\text{NH}_3, \text{MoO}_2\text{SO}_3, 7\text{MoO}_3, 10\text{H}_2\text{O}$, in dark blue prisms ; the latter is converted into the former by the further action of ammonia. Both these compounds are very soluble in water, but insoluble in solutions of ammonium salts ; they are only very slowly decomposed by alkalis or nitric acid at the ordinary temperature, and are therefore more stable than the other blue compounds of molybdenum which have been described. Analogous compounds containing potassium, and both potassium and ammonium, have also been obtained, but the corresponding sodium salt is too soluble to admit of isolation.

The prolonged reduction of molybdic acid by alcohol at the ordinary

temperature results in the formation of a *compound* which crystallises in slender, black needles and has possibly the composition



whilst if the operation is effected at 100° , solutions are obtained which, when cooled, are immediately decomposed by ammonia. N. L.

Tungsten. By EDOUARD DEFACQZ (*Ann. Chim. Phys.*, 1901, [vii], 22, 238—288).—A detailed account of a series of contributions to the chemistry of tungsten. The results have, however, already been published (compare *Abstr.*, 1897, ii, 77, 163, 214; 1898, ii, 521; 1899, ii, 159, 428, 489, 754; 1900, ii, 350; this vol., ii, 105). Traces of tungsten are most readily detected by fusing the substance under examination with potassium hydrogen sulphate, treating the fused mass with dilute sulphuric acid, and adding to the extract a few drops of phenol or quinol solution; the former reagent develops a red, and the latter a violet, coloration. The phenols in general, and also many of the alkaloids, give characteristic reactions with acid solutions of tungstic acid. G. T. M.

New Method of Determining the Atomic Weight of Uranium. By JULES ALOY (*Compt. rend.*, 1901, 132, 551—553).—The atomic weight of uranium may be easily and accurately determined by estimating the relative proportions of nitrogen and the metal in the carefully purified nitrate. The nitrogen is estimated by a modification of Dumas' method, and the uranium is weighed as the dioxide, UO_2 , obtained by reducing in a current of hydrogen the residue left on to calcining the nitrate in the preceding estimation. It is advantageous to employ in this estimation the nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, obtained by partially dehydrating the hexahydrate in a desiccator, under diminished pressure. Assuming that the atomic weight of nitrogen is 14.04, the mean of seven concordant determinations of the atomic weight of uranium is 239.4. G. T. M.

Enantiotropy of Tin. VI. By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 469—472).—Classical authors, for instance, Aristotle, appear to have been aware of the changes which tin may undergo at low temperatures. L. M. J.

Double Compounds of Quadrivalent Titanium. By ARTHUR ROSENHEIM and OTTO SCHÜTTE (*Zeit. anorg. Chem.*, 1901, 26, 239—257).—Titanium tetrachloride or hydroxide dissolves in fuming hydrochloric acid, forming a deep yellow solution. Alcoholic or ethereal solutions of hydrochloric acid also dissolve the hydroxide readily, and when the ethereal solution is evaporated a microcrystalline, yellowish residue is obtained, which may be washed with ether, but cannot be dried without decomposition. It appears to be either $\text{TiCl}_3 \cdot \text{Et}_2\text{O}$, or $\text{TiCl}_3 \cdot \text{OH} \cdot \text{Et}_2\text{O}$.

Ammonium titanichloride, $(\text{NH}_4)_2\text{TiCl}_6 \cdot 2\text{H}_2\text{O}$, is obtained by shaking the solution of titanium tetrachloride in fuming hydrochloric acid with the theoretical quantity of ammonium chloride for 12 hours in the cold and washing with ether. It is a yellow, crystalline substance which very readily loses hydrochloric acid in moist air.

Pyridine titanichloride, $(\text{C}_5\text{H}_5\text{N})_2 \cdot \text{H}_2\text{TiCl}_6$, is deposited in yellow

crystals from a solution of pyridine hydrochloride, and titanous chloride in hydrochloric acid. It decomposes when exposed to air or dissolved in water.

Quinoline titanichloride, $(C_9H_7N)_2, H_2TiCl_6$, is more stable than the foregoing compound.

Aniline titanichloride, $(NH_2Ph)_4, H_4TiCl_6$, obtained in the same way, is fairly stable in the air.

Ammoniotitanium tetrachloride, $TiCl_4, 6NH_3$, is an amorphous, dark yellow powder obtained by passing dry ammonia into an ethereal solution of titanium tetrachloride; it loses ammonia in presence of dry calcium chloride, and becomes almost colourless, the residue having the composition $TiCl_4, 4NH_3$. Both compounds are very unstable in presence of moist air.

Titanium tetrachloride pyridine, $TiCl_4, 6C_5H_5N$, was obtained in the same way as the analogous ammonia compound.

Solutions of hydrobromic acid in water, alcohol, or ether dissolve titanium tetrabromide or hydroxide, yielding dark red liquids. From the ethereal solution, a crystalline substance was obtained, which was too unstable to permit of analysis. When evaporated in a vacuum, the alcoholic solution deposits a colourless, crystalline powder, which is stable when exposed to air, and appears to be $TiBr(OH)_3, 1\frac{1}{2}H_2O$.

The solution in aqueous hydrobromic acid gives a crystalline compound with ammonium bromide, which is much less stable than the corresponding chloride.

Pyridine titanibromide, $(C_5H_5N)_2, H_2TiBr_6$, is obtained by saturating with hydrogen bromide a solution containing pyridine hydrobromide and titanous acid dissolved in alcoholic hydrogen bromide. This solution, when it is not treated with hydrogen bromide, deposits crystals of $3(C_5H_5N, HBr), TiOBr_2$.

The iodine analogues of the compounds above described could not be prepared owing to their great instability.

A solution of titanium tetrachloride in ether acts on lead thiocyanate, yielding what appears to be a titanium salt of a polymeric thiocyanic acid.

Titanium sulphates.— $TiOSO_4, 5H_2O$, is obtained by boiling titanous hydroxide with alcoholic sulphuric acid and evaporating the alcohol or precipitating with excess of ether. The salt, $2K_2SO_4, 3TiOSO_4, 10H_2O$, is deposited in colourless needles when a concentrated aqueous solution of potassium sulphate is added to a saturated solution of titanous acid in concentrated sulphuric acid. The ammonium salt, $(NH_4)_2SO_4, TiOSO_4, H_2O$, is obtained similarly.

Titanium Oxalates.—Concentrated solutions of acid ammonium oxalate dissolve titanous acid, forming the salt $TiO(C_2O_4NH_4)_2, H_2O$, which crystallises in large, transparent, monoclinic crystals. The oxalate, $TiOC_2H_4, Et \cdot OH$, is obtained as a white, crystalline precipitate readily soluble in water or alcohol by boiling titanous acid with alcoholic oxalic acid and precipitating the solution with ether. The compound $C_2O_4(TiO)_2, 12H_2O$ is obtained by adding a concentrated solution of oxalic acid to a solution of titanous hydroxide in hydrochloric acid and precipitating with alcohol. It is insoluble in water and sparingly soluble in dilute acids.

Titanium Tartrates.—Hot concentrated solutions of acid alkali tartrates dissolve precipitated titanium hydroxide readily. The solutions solidify, when concentrated, to gelatinous substances possessing the composition $2R_2O, 2TiO_2, 3C_4H_4O_6, xH_2O$, x being 6 for the potassium and 10 for the sodium and ammonium salts. The salt, $Ti(C_4H_4O_6)_2 \cdot 4H_2O$, was obtained by saturating a concentrated aqueous solution of tartaric acid with titanium hydroxide and evaporation. It formed a syrup which was dried on porous earthenware. Its solutions are characterised by their high specific rotatory power, a solution of 1.5 grams in 100 c.c. giving $[\alpha]_D 140.8^\circ$ at 15° .

When a solution of titanic acid in hydrochloric acid is treated with tartaric acid and a large excess of alcohol, a white, amorphous precipitate is obtained of the compound $C_4H_4O_6(TiO)_2 \cdot 7H_2O$. It is insoluble in water, but readily soluble in dilute acids or ammonia.

T. E.

Platinum Compounds. By ARTURO MIOLATI and I. BELLUCCI (*Gazzetta*, 1900, 30, ii, 588—596).—The authors have made several unsuccessful attempts to prepare compounds of the composition $PtX_4(OH)_2H_2$, X representing CN, CNS, or NO_2 .

Silver dichloroplatinicyanide, $Ag_2(PtCl_2Cy_4)_2$, obtained in the form of a pale yellow precipitate, is not decomposed by heating with water under pressure or by the action of chlorine. The corresponding dibromo- and diiodo-salts, forming respectively yellow and chestnut precipitates, behave in a similar manner towards water.

Bromine acts on potassium platothiocyante according to the equation: $2Pt(CNS)_4K_2 + Br_2 = Pt(CNS)_6K_2 + Pt(CNS)_2 + 2KBr$.

The reaction between potassium platinithiocyanate and platinibromide gives rise to platinous thiocyanate and potassium bromide.

Silver platininitrobromide, $Pt(NO_2)_4Br_2Ag_2$, is obtained as a red precipitate which is too unstable to allow of the bromine atoms being replaced by hydroxyl groups.

T. H. P.

Some Ruthenium Compounds. By ARTURO MIOLATI and C. C. TAGIURI (*Gazzetta*, 1900, 30, ii, 511—529).—When chlorine acts on a mixture of sodium chloride and ruthenium chloride, and the product of the reaction is lixiviated with water, a dark red liquid is obtained, containing probably sodium ruthenichloride. If the solution be hot and dilute or be placed in contact with organic substances, it becomes more brown in colour and is found to contain ruthenium trichloride, since the addition of potassium chloride precipitates the compound of the composition $K_2RuCl_5 \cdot H_2O$, whilst evaporation of the mother liquors yields the substance K_2RuCl_5 .

On boiling together solutions of sodium ruthenochloride (Na_2RuCl_5) and sodium hydrogen sulphite, a minute, crystalline precipitate of the composition $Na_7Ru(SO_3)_5 \cdot 2H_2O$, is obtained. The corresponding potassium compounds give, after the addition of aqueous potassium hydroxide, a blue compound of the composition $O[Ru(SO_3)_4K_6]_2 \cdot 4H_2O$.

The action of sodium hydrogen sulphite on sodium rutheninitrosochloride yields the compound $O[Ru(SO_3)_2(NO)Na_2]_2 \cdot 2H_2O$, which separates in the form of minute, orange-yellow crystals slightly

soluble in cold water. The corresponding *potassium* compound separates in minute needles also containing $2\text{H}_2\text{O}$.

For the analysis of these complex salts, the authors have devised special methods, of which a full description is given. T. H. P.

Ruthenium and its Compounds. By UBALDO ANTONY and ADOLFO LUCCHESI (*Gazzetta*, 1900, 30, ii, 539—544).—*Ruthenium trisulphide*, RuS_3 , is obtained as a yellowish-brown precipitate when hydrogen sulphide is passed into a solution of potassium ruthenichloride kept at 0° . In the dry state, the sulphide is readily oxidised in the air and becomes heated to incandescence, so that it is necessary to dry it in an atmosphere of carbon dioxide.

If the hydrogen sulphide and potassium ruthenichloride react at $80\text{--}90^\circ$, ruthenium disulphide is obtained as a black precipitate which must be dried in the same way as the trisulphide. When gently heated in presence of air, even although the latter be diluted with nitrogen, a violent explosion occurs. T. H. P.

Mineralogical Chemistry.

Analysis of Tetrahedrite from Mount Botes, Hungary. By JOZSEF LOCZKA (*Zeit. Kryst. Min.*, 1901, 34, 81—87).—The following results, the mean of two analyses, were obtained with tetrahedral crystals of tetrahedrite, of which a crystallographic description is given by K. Zimányi in an accompanying paper (*ibid*, 78—83). The streak is dark brownish-black; on the bright, uneven fracture no impurities could be seen. Sp. gr. 4·968.

| S. | Sb. | As. | Cu. | Ag. | Pb. | Fe. | Mn. |
|-------|-------|------|--------|--------|------|------|------|
| 25·16 | 26·61 | 0·38 | 37·22 | 1·51 | 0·33 | 0·80 | 0·69 |
| | | Zn. | Insol. | Total. | | | |
| | | 6·59 | 0·06 | 99·35 | | | |

No simple formula can be deduced from these figures (compare Abstr., 1900, ii, 21). L. J. S.

Strontianite from Münster-land. By JOSEPH BEYKIRCH (*Jahrb. Min.*, 1901, *Beil.-Bd.*, 13, 389—433).—A description is given of the strontianite which occurs with calcite in veins in chalk-marl at various localities in Westphalia. In seventeen new analyses the constituents vary as follows: SrCO_3 , 88·69—94·29; CaCO_3 , 5·61—11·12; traces of ferrous carbonate and silica are sometimes present. Sp. gr. 3·628—3·728. Analyses are also given of “calcistrontianite” (compare Abstr., 1896, ii, 660). Detailed crystallographic and optical determinations are also given [$a:b:c = 0·60903:1:0·72399$]. There appears to be a connection between the slight variation in the divergence of the optic

axes and the amount of calcium carbonate present; the latter, therefore, probably replaces strontium carbonate isomorphously.

L. J. S.

Dolomite [Ankerite] from Magdeburg. By JOHANNES FAHRENHORST (*Zeit. Naturwiss.*, 1900, 73, 275—279).—A mineral referred to dolomite occurs with calcite, barytes, pyrites and copper-pyrites in crevices in greywacke at Ebendorf near Magdeburg. Analysis I is of colourless, translucent rhombohedra with $rr' = 73^{\circ}50'$; and II of small curved rhombohedra with a pearly lustre. [This composition points to ankerite rather than dolomite.]

| | CaO. | FeO. | MgO. | MnO. | SiO ₂ . | Sp. gr. |
|-----|-------|-------|-------|------|--------------------|---------|
| I. | 28.69 | 14.01 | 11.95 | 0.86 | 0.16 | 2.96 |
| II. | 31.95 | 10.71 | 10.53 | 2.37 | 0.08 | — |

L. J. S.

Phosphates from Moravia. By CONRAD H. VON JOHN (*Chem. Centr.*, 1901, i, 417; from *Verh. geol. Reichsanst., Wien*, 1900, 337—340).—The minerals analysed occur in cavities in pegmatite at Cyrillhof near Gross-Meseritsch in Moravia; they are mixtures to which it would not be advisable to give special names. I is dark brown and amorphous with a sub-conchoidal fracture and a greasy lustre; it is very similar to triplite, but differs in containing no fluorine; the composition may be represented by $9R''_3P_2O_8 + (R_2O_3)_3(P_2O_5)_2$. II is black with a conchoidal fracture and greasy lustre. III is dark blackish-brown with an irregular earthy fracture.

| | P ₂ O ₅ . | Al ₂ O ₃ . | FeO. | Fe ₂ O ₃ . | MnO. | CaO. | MgO. | K ₂ O. |
|------|---------------------------------|----------------------------------|-------|----------------------------------|-------|------|------|-------------------|
| I. | 39.65 | 0.46 | 26.09 | 9.51 | 18.18 | 3.86 | 0.07 | 0.81 |
| II. | 32.50 | — | 0.36 | 26.66 | 28.66 | 2.68 | — | — |
| III. | 31.60 | — | 3.09 | 27.91 | 26.83 | 2.82 | — | — |

| | Na ₂ O. | Cl. | SiO ₂ . | H ₂ O. | Total. |
|------|--------------------|------|--------------------|-------------------|--------|
| I. | 1.12 | 0.14 | — | — | 99.89 |
| II. | — | — | 0.62 | 9.12 | 100.60 |
| III. | — | — | — | 9.16 | 101.41 |

L. J. S.

Triplite from Moravia. By CONRAD H. VON JOHN (*Chem. Centr.*, 1901, i, 416; from *Verh. geol. Reichsanst., Wien*, 1900, 335—337).—Massive, dark brown triplite was found in a nest in pegmatite at Wien near Gross-Meseritsch in Moravia. It is frequently intergrown with large plates of muscovite. On the fresh sub-conchoidal fracture it has a greasy lustre. Analysis gave:

| F. | P ₂ O ₅ . | FeO. | MnO. | CaO. | MgO. | K ₂ O. | Na ₂ O. | Total. |
|------|---------------------------------|-------|-------|------|-------|-------------------|--------------------|--------|
| 8.17 | 31.29 | 31.03 | 31.05 | 1.42 | trace | 0.72 | 0.52 | 104.20 |

This agrees with the usual formula, $R_3P_2O_8.RF_2$, with Fe : Mn = 1 : 1.

L. J. S.

Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XIX. Maximum Vapour Pressure at 25° o Solutions of the Chlorides and Sulphates of Magnesium and Potassium, the Solutions being Saturated with Sodium Chloride: the Formation of Kainite at 25°. By JACOBUS H. VAN'T HOFF and H. VON EULER-CHELPIN (*Sitzungsber. Akad. Wiss. Berlin*, 1900, 1018—1022. Compare Abstr., 1900, ii, 23).—The contents of the paper are indicated by the title. The results obtained are considered in connection with the order in which various salts separate out on the evaporation of sea water (*loc. cit.*). J. C. P.

Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XX. Formation of Syngenite at 25°. By JACOBUS H. VAN'T HOFF and HAROLD A. WILSON (*Sitzungsber. Akad. Wiss. Berlin*, 1900, 1142—1149).—The conditions of formation of syngenite, $\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, have been studied on the same lines as were followed in the case of glauberite (Abstr., 1900, ii, 284). Syngenite is obtained by shaking gypsum with a sufficiently concentrated solution of potassium sulphate, but is decomposed on contact with water or a dilute solution of potassium sulphate. The conditions of the existence of syngenite at 25° have been studied (1) in solutions containing no magnesium, (2) in solutions containing magnesium; in the latter case, matters are complicated by the possible formation of polyhalite, $\text{Ca}_2\text{K}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$. The results are treated graphically, and do not lend themselves to abstraction. J. C. P.

Theory of Silicates. By W. VERNADSKY (*Zeit. Kryst. Min.*, 1901, 34, 37—66).—The author divides the silicates into two main groups, (A) "simple" silicates containing no sesquioxides and (B) aluminosilicates (including ferrisilicates, borosilicates and chromosilicates); these are subdivided as shown below. The following may be given as examples of the term "additive product": hemimorphite ($\text{Zn}_3\text{SiO}_4 \cdot \text{H}_2\text{O}$) is considered as an additive product of calamine (Zn_2SiO_4), and in serpentine there is the addition of a metasilicate portion to an orthosilicate "nucleus."

A. Simple silicates.

I. Hydrates. Opal group.

II. Salts.

a. Orthosilicates.

1. Salts. Olivine, troostite and sepiolite groups.

2. Additive products. Chondrodite, serpentine, chrysocolla, noumeaite and calamine groups.

b. Metasilicates.

Pyroxene (and amphibole), talc and apophyllite groups.

B. Aluminosilicates.

I. Complex anhydrides and additive products. Sillimanite group.

II. Complex acids (hydrates) and additive products. Clay group.

III. Complex salts and additive products.

a. Salts with "chlorite nucleus," Staurolite, clintonite, chlorite and melilite groups.

b. Salts with "mica nucleus." Mica, leucite, felspar, petalite, nepheline, carpholite, scapolite, epidote, garnet, idocrase, prehnite and zeolite groups.

Each of the above groups is discussed in detail, and structural formulæ are given. The following groups form an appendix to the classification. C, beryllium silicates. D, borosilicates; *a*, simple borosilicates, *b*, borosilicates. E, cerium and yttrium silicates. F, Titanosilicates. G, zirconosilicates. H, uranosilicates.

L. J. S.

[Enstatite from Massachusetts.] By BENJAMIN KENDALL EMERSON (*Jahrb. Min.*, 1901, i, Ref. 36; from *Monograph U.S. Geol. Survey*, 1898, 29, 754—761).—Supplementary notes are given on the minerals of Franklin, Hampshire, and Hampden counties, Massachusetts (Abstr., 1897, ii, 566). The following analysis by Hillebrand is given of large, colourless prisms of slightly altered enstatite from the serpentine of Granville:

| SiO ₂ . | Al ₂ O ₃ . | Cr ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | NiO. | MnO. | MgO. |
|--------------------------------------|----------------------------------|----------------------------------|----------------------------------|--------------------------|------|-------------------|-------|
| 54·04 | 0·52 | 0·14 | 1·51 | 3·90 | 0·23 | 0·11 | 34·40 |
| K ₂ O, Na ₂ O. | | H ₂ O < 110°. | | H ₂ O > 110°. | | CO ₂ . | |
| 0·08 | | 0·70 | | 3·07 | | 100·02 | |

L. J. S.

Chloropal from Moravia. By CONRAD H. VON JOHN (*Chem. Centr.*, 1901, i, 416; from *Verh. geol. Reichsanst., Wien*, 1900, 340—341).—Yellowish-green, earthy or compact chloropal occurs at Gdossau and Pulitz near Jamnitz in Moravia. The following analysis gives the usual formula, Fe₂Si₃O₉·5H₂O.

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | MgO. | H ₂ O. | Total. |
|--------------------|----------------------------------|----------------------------------|------|------|-------------------|--------|
| 41·80 | 0·91 | 35·29 | 1·04 | 0·92 | 20·36 | 100·32 |

L. J. S.

New Mineral Occurrences in Canada. By G. CHRISTIAN HOFFMANN (*Amer. J. Sci.*, 1901, [iv], 11, 149—153).—Lepidolite occurs as large plates, up to 28 inches across, in a coarse granite vein in the township of Wakefield, Ottawa Co., Quebec. Thin laminæ are transparent and colourless, but thick plates are purplish-brown. Sp. gr. 2·858. Analysis by R. A. A. Johnston gave:

| | | | | | | |
|--------------------|----------------------------------|----------------------------------|------|---------------|-------------------|--------------------|
| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | MnO. | MgO. | K ₂ O. | Na ₂ O. |
| 47·89 | 21·16 | 2·52 | 4·19 | 0·36 | 10·73 | 1·34 |
| Total. | | | | | | |
| Li ₂ O. | | H ₂ O. | | less O for F. | | |
| 5·44 | | 1·90 | | 99·82 | | |

A colourless, transparent substance from the interspaces in the ivory of the tusk of a fossil mammoth found in the Yukon district, Northwest Territory, gave on analysis by Johnston:

| P ₂ O ₅ . | MgO. | NH ₃ . | CO ₂ | H ₂ O. | Total. |
|---------------------------------|-------|-------------------|-----------------|-------------------|--------|
| 38·53 | 21·93 | 1·94 | 0·42 | [37·18] | 100·00 |

This composition is explained by assuming that the substance is a mixture of two mols. of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) with one of newberyite ($\text{HMgPO}_4 \cdot 3\text{H}_2\text{O}$) and a little magnesite.

A massive velvet-black mineral occurring in considerable masses as an accessory constituent in the nepheline syenite of the Ice River, British Columbia, is shown by the following analysis by F. G. Wait to be schorlomite. Sp. gr. 3.802. In the figures given below, TiO_2 , TiO , Fe_2O_3 and FeO have been recalculated to agree with the garnet formula.

| SiO_2 | TiO_2 | Al_2O_3 | Fe_2O_3 | TiO | MnO | CaO | MgO | Total. |
|----------------|----------------|-------------------------|-------------------------|--------------|--------------|--------------|--------------|--------|
| 25.77 | 10.83 | 3.21 | 18.59 | 8.23 | 0.76 | 31.76 | 1.22 | 100.37 |

Danalite, spodumene and uranophane are also described.

L. J. S.

Recalculation of Rock Analyses. By JAMES FURMAN KEMP (*School of Mines Quart., New York*, 1900, 22, 75—88).—Tables are given for finding the molecular ratios of the various constituents shown in percentage analyses of rocks. A worked example shows the method of calculating the mineralogical composition from the percentage chemical composition.

L. J. S.

Rocks from the Newlands Diamond Mines, S. Africa. By THOMAS GEORGE BONNEY (*Proc. Roy. Soc.*, 1901, 67, 475—484. Compare Abstr., 1899, ii, 769).—A description is given of another small collection of rock specimens from this locality. An analysis is given of a specimen of the "blue ground" which contains an unusual abundance of minute scales of brown mica. Microscopic diamonds have been found in the eclogite described in the previous paper. L. J. S.

Cosmic Diffusion of Vanadium. By CLAS BERNHARD HASSELBERG (*Öfvers. Svenska. Vetensk. Akad. Förhandl.*, 1899, 56, 131—140. Compare Abstr., 1898, ii, 30).—A number of meteorites, fallen in various parts of the world, have been examined spectroscopically for the presence of vanadium. Of the 31 specimens investigated, it was found that all those of the stony type contain small proportions of vanadium, which was, however, only detected in one metallic meteorite, and then only in very small quantity. This fact seems to indicate a different origin for stony and for metallic meteorites. The observation of Lockyer (*Phil. Trans.*, 1894, 185, 1023) of the presence of vanadium in specimens of meteoric iron from Nejed and Obernkirchen is erroneous, since of the four lines given by him as belonging to vanadium, only two approximate to lines of this metal, besides which no trace appears of the principal group of vanadium lines with $\lambda = 4408$ —4379. Further, the author has directly compared the spectra of the Nejed meteorite and of vanadium, and failed to discover in the former the lines given by Lockyer.

T. H. P.

Granular and Compact Meteoric Irons. By EMIL W. COHEN (*Sitzungsber. Akad. Wiss. Berlin*, 1900, 1122—1135).—A summary is given of the author's several recent papers on meteoric irons, of which

the structure is compact or granular (ataxites). A comparison of the analyses shows that, with few exceptions, there is a close relation between structure and chemical composition, as is also the case in other groups (hexahedrites and octahedrites) of meteoric irons.

L. J. S.

Analysis of the Mineral Water of the Cévennes Spring at Ucel (Ardèche). By ETIENNE BARRAL (*Bull. Soc. Chim.*, 1901, [iii], 25, 257—259).—This water has a temperature of 16°, contains 134 c.c. of free carbon dioxide per litre, and yields a solid residue of 2.357 grams per litre, consisting chiefly of magnesium and sodium sulphates and sodium and calcium carbonates.

N. L.

Occurrence of Barium in the Spring Water of Boston Spa. By PERCY A. E. RICHARDS (*Analyst*, 1901, 26, 68—70. Compare White, *Abstr.*, 1899, ii, 420).—The author has found that the spring water of Boston Spa contains the remarkably large amount of 41 parts of barium chloride per 100,000. The presence of this salt has not been in the least suspected during the last 100 years. Full analyses of the water are given.

L. DE K.

Physiological Chemistry.

Gastric Digestion in Selachian Fishes. By ERNST WEINLAND (*Zeit. Biol.*, 1901, 41, 35—68).—The food remains in the stomach of the dogfish, torpedo, and ray, if the animals are kept at 13—15°, 2, 3, or more (in one case 18) days. The gastric juice of dogfish and torpedo is always acid; in dead and moribund animals, it is alkaline. In the ray, it is sometimes acid, sometimes alkaline; an alkaline secretion can always be artificially obtained in this animal, but not in the other two, by subcutaneous injection of extract of *Secalis cornuti*. This drug causes a contraction of the vessels of the mucous membrane to such an extent that the circularly arranged fibres form sphincters which prevent the blood flowing. W. D. H.

Cellulose Digestion in the Alimentary Canal. By ERICH MÜLLER (Berlin) (*Pflüger's Archiv*, 1901, 83, 619—627).—Several previous workers (Knauthe; Biedermann and Moritz, *Abstr.*, 1898, ii, 166, &c.) have stated that a cellulose-dissolving enzyme occurs in the secretion of the hepato-pancreas of certain invertebrates. In the present experiments, paper was employed, but a loss of paper and a formation of sugar were never found, and the search for a cellulose-dissolving enzyme was entirely negative. Indeed, in control experiments, in which the secretion and alkaline solution were alone used without the paper, more sugar was often found than in the experiments where paper was added. W. D. H.

Digestion of Food by Man. By WIEBUR O. ATWATER and FRANCIS G. BENEDICT (10th *Ann. Rep. Storrs's Agr. Exper. Stat.* for 1897, 154—167).—The observations are part of a series of metabolism experiments with respiration calorimeter (compare *ibid.*, No. 9, 1896, 163). During a preliminary experiment, the body was brought into approximate equilibrium with the food, and the muscular activity was made as similar in amount as possible to that of the second period. At the last meal of the day previous to the commencement of each experiment, animal charcoal was consumed, to enable the separation of the fæces of the experimental period to be effected. Samples of the dried food, fæces, and urine were burned in the bomb calorimeter.

The actual fuel value of food is considered to be the heat of combustion of the portion oxidised (or oxidisable) in the body, or the heat of combustion of the total food less the heats of combustion of the un-oxidised excrementitious matters.

It is pointed out that what is usually termed the digestibility of foods would be more correctly designated availability.

The results relating to the various foods are given in tables.

N. H. J. M.

Digestibility of Butter and its Substitutes. By H. WIBBENS and H. E. HUIZENGA (*Pflüger's Archiv*, 1901, 83, 609—618).—The digestibility of butter is contrasted by actual feeding experiments with those of "sana" and "margarine." Of the three, "sana" is least absorbable, but the differences between the two kinds of fat is so small as to be almost negligible.

W. D. H.

Lipase. By A. S. LOEVENHART (*Proc. Amer. Physiol. Soc.*, 1900, xii—xiii. Compare this vol., i, 178).—The degree of activity in any organ is related to the amount of fat transformation taking place there; thus the resting mammary gland possesses but a trace of activity, but when active, its lipolytic power is equal to that of the pancreas. The occurrence of lipase in subcutaneous fat explains why inanition fat is absorbed from this region, and its reversible action accounts for the storage that takes place at other times.

W. D. H.

Metabolism in Forced Feeding. By W. HALE WHITE and E. I. SPRIGGS (*J. Physiol.*, 1901, 26, 151—165).—A full account of the experiment previously recorded (this vol., ii, 28). The deficit of nitrogen in the output is reduced by careful allowance for all possible channels of excretion to 120 grams, or about 5 per cent. of the amount injected, but as some of the increase of weight in the patient was no doubt fat, the correct figure is probably nearer 10. The deficit is perhaps explicable on the assumption that a considerable quantity of simpler nitrogenous substances (creatine, &c.) was formed and retained in the body, and, further, that in overfeeding, the tissues contain less water than in health. If this were so, the figures would come out differently, for the calculations in the paper are made on the assumption that the tissues were normal.

W. D. H.

Influence of Drugs on Hepatic Metabolism. By DIARMID NOEL PATON and J. EASON (*J. Physiol.*, 1901, 26, 166—172).—The

few experiments recorded suggest the following conclusions. Certain drugs (sulphonal, alcohol, carbon monoxide given as coal gas) lessen the amount of waste nitrogen elaborated into the form of urea. Certain other drugs (quinine, morphine) have not this action. The percentage of oxidised sulphur in the urine varies in a corresponding way. The effect is probably related to the activity of liver metabolism. Morphine diminishes the ratio of phosphorus to nitrogen in the urine, whilst carbon monoxide (as coal gas) has not this action.

W. D. H.

The Cause of the Increase of Proteid Decomposition during Inanition. By MARTIN KAUFMANN (*Zeit. Biol.*, 1901, 41, 75—112).—The increase in nitrogenous katabolism often observed during inanition can be prevented in rabbits by giving sugar, and when it does occur it is due to the poorness of the body in proteid-sparing fat.

W. D. H.

The Need for Energy in Animals during Inanition. By ERWIN VOIT (*Zeit. Biol.*, 1901, 41, 113—154).—Rubner's law regarding the energy-need and surface area of animals holds only during rest, when the animal is kept in a mean external temperature and in a normal nutritive condition, but does not hold in comparisons between animals in different nutritive conditions. During inanition, there is no proportion between need of energy and surface area, but the former sinks as the proteid material wastes. If the relationship between energy-need and cell mass is considered as a function of the hunger period, a curve is obtained which, after a short fall, becomes horizontal.

W. D. H.

Influence of Foods on Muscular Work. By H. NEWTON HEINEMANN (*Pflüger's Archiv*, 1901, 83, 441—476). **The Source of Muscular Energy.** By JOHANNES FRENTZEL and FELIX REACH (*ibid.*, 477—508). **Proteid Metabolism and Muscular Work.** By WILHELM CASPARI (*ibid.*, 509—539). **Proteid Feeding and Muscular Work.** By KARL BORNSTEIN (*ibid.*, 540—556). **General Conclusions.** By NATHAN ZUNTZ (*ibid.*, 557—571).—A series of five papers on the much discussed question of the source of muscular energy. Some, like Pflüger, maintain that proteid decomposition is the main source, whilst others attribute it to sugar or other non-nitrogenous materials. Zuntz has shown that the rise of the respiratory quotient, noted by some and regarded by them as a proof that carbohydrate katabolism accounts for the energy produced, does not really occur if all sources of fallacy in method are excluded. Zuntz's own theory is, that any exclusive rôle for any particular class of food substances is incorrect, but allowing for the proteid-sparing action of fats and carbohydrates, the energy-producing power of any variety of food is proportional to its calorific value. Many of the present series of papers traverse the same ground in the discussion of previous work and results, and the final paper by the investigator under whose direction the work has been done is an attempt to coordinate the results, which confirm the theory just stated. The work appears to have been most laborious, extending in many cases to months of observation, and the experimental

results are given with full details. The first two papers deal with results on man on various diets, in the first case using a machine from which the work could be easily calculated, whilst in the second case, walking was the exercise selected. The next two papers deal more with proteid nutrition, the first on dogs, the second on patients undergoing the Weir Mitchell cure with excess of proteid food. They seek to explain the increase of weight, especially in muscle (noted also during athletic training), which occurs in spite of muscular work of an extreme kind.

W. D. H.

Composition and Heat Value of the Muscular Substance from different Animals. By A. KÖHLER (*Zeit. physiol. Chem.*, 1901, 31, 479—519).—The bulk of the paper is occupied with analytical tables of the composition of the muscular tissue of the animals commonly used as food. The elementary composition of this tissue when free from water, ash, and fat does not appear to differ much; the calorific value varies from 5599 to 5677 cal. The fat analyses given were made by Dormeyer's method. The amount of glycogen in horse-flesh is given as 3.58 to 3.72 per cent.

W. D. H.

Does Muscle contain Mucin? By G. A. FRIED and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1900, x—xi).—After allowing for alkali-albumin, which is precipitable by acid and soluble in excess, only a faint turbidity suggested traces of mucin.

W. D. H.

Proteids of Unstripped Muscle. By SWALE VINCENT and THOMAS LEWIS (*Proc. Physiol. Soc.*, 1901, xix—xxi).—Rigor mortis, accompanied by slight acidity, occurs in the plain muscle of the stomach, and rectum. Extracts are neutral or alkaline; they contain little or no paramyosinogen, but abundance of myosinogen.

W. D. H.

Effect of Carbon Dioxide and Oxygen on Smooth Muscle. By ALLEN CLEGHORN and H. D. LLOYD (*Proc. Amer. Physiol. Soc.*, 1900, xvi).—Carbon dioxide increases the tissues of smooth muscle from the frog's stomach, but eventually stops the contractions. Recovery was not accelerated by the application of oxygen.

W. D. H.

The Action of Iodine and Iodides on Frog's Muscles. By RALPH STOCKMAN and FRANCIS J. CHARTERIS (*J. Physiol.*, 1901, 26, 277—281).—Iodine, chlorine, and bromine cause rigor mortis and an acid reaction to appear in frog's voluntary muscles; the heart is killed later. The spinal cord and nerves remain excitable so long as the muscles respond. Iodides have also this effect, but chlorides and bromides have it, if at all, only to a very slight degree. After subcutaneous injection, the muscles near the seat of injection are affected first. The iodides of potassium and ammonium have a more powerful action than that of sodium. It is probable that the action is due to liberation of free iodine, and the small effect of chlorides and bromides is due to their being more stable salts. In rabbits, the voluntary muscles are not affected, but the occurrence of lung œdema and pleurisy points to irritation, possibly again due to free iodine.

W. D. H.

Hibernation in Bats. By HECTOR RULOT (*Bull. Acad. Roy. Belg.*, 1901, 17—50).—Although there is absolute loss of water at the end of the winter sleep in bats, there is a proportional increase. Both the absolute and relative weights of fat diminish from the commencement to the end of the winter, especially in the later months. The glycogen follows the same rule, slightly increasing, however, in the last months of the sleep. The amounts of glycogen are throughout so small that this material can hardly be considered to be an important store of material. The consumption of proteid is more marked in the later than in the earlier months, but the relation between the amounts of proteid and fat destroyed rises considerably during April, the last month of the sleep. The sleep is most profound at the beginning of the winter, but the amount of carbon burnt increases from November to April.

W. D. H.

[**Osmotic Phenomena of Red Blood Corpuscles.**] By R. QUINTON (*Compt. rend.*, 1901, 132, 347—350, 432—434).—The non-nucleated red corpuscle offers no resistance to the passage of urea into its protoplasm. The nucleated red corpuscle resists this penetration, and osmotic equilibrium can be established. In this, the nucleated red corpuscle resembles vegetable cells.

W. D. H.

Mechanism of the Action of the [Red] Blood Corpuscles. By PIERRE NOLF (*Ann. Inst. Pasteur*, 1900, 14, 656—685).—The reagents which effect the action of blood corpuscles do so because they increase the affinity of the cell wall for water. The alexins are not proteolytic ferments, but act like the chemical reagents, which cause hæmolysis.

R. H. P.

Blood taken from Animals deprived of their Suprarenals. By ISAAC LEWIN (*Proc. Amer. Physiol. Soc.*, 1900, ix).—The blood of an animal from which the suprarenals have been removed produces when injected intravenously into another animal a rise of blood pressure. Normal blood has no such effect. The substance or substances to which this is due must therefore under ordinary conditions be neutralised by the suprarenals.

W. D. H.

Fibrinolysis. By L. CAMUS (*Compt. rend.*, 1901, 132, 215—218).—If fibrin suspended in salt solution is injected into the peritoneal cavity of rabbits, the serum of the blood is found to have lost its fibrinolytic activity. Injection of serum leads to a corresponding result, but the globulins of the serum do not have this effect. The albumins were not tried. The serum of such immunised animals precipitates solutions of fibrin prepared from the blood of animals of the same kind; this precipitate is redissolved by normal serum.

W. D. H.

Origin of the Alexin of Normal [Blood] Serums. By O. GENGOU (*Ann. Inst. Pasteur*, 1901, 15, 68—84).—Alexin is found in larger quantity in the polynuclear leucocytes than in normal blood serum of dogs and rabbits, whilst the white corpuscles with a single nucleus contain only small quantities. It therefore appears that the

polynuclear leucocytes are the source of the alexin which is found in normal blood serum. R. H. P.

Action of Chloroform on the Reducing Power of Blood. By M. LAMBERT and LÉON GARNIER (*Compt. rend.*, 1901, 132, 493—495).—When defibrinated blood is treated with a current of air containing chloroform vapour, the reducing power of the blood is sometimes increased at once, and always after an hour, and this increased reducing power is not due to the dissolution of chloroform in the blood. When, however, defibrinated blood and similar blood containing chloroform are made to circulate respectively through the two lobes of a fresh liver, the glycogen disappears more rapidly in the lobe through which the blood containing chloroform circulates and at the same time the reducing power of this blood increases more rapidly than that of the pure blood, and in a higher degree than corresponds with the glycogen that disappears. It follows that the increased reducing power is not due simply to a more active formation of sugar or to a diminution in its rate of consumption. C. H. B.

Effect of Ions on the Contraction of the Lymph Hearts of the Frog. By ANNE MOORE (*Amer. J. Physiol.*, 1901, 5, 87—94).—The rhythmical contractions of the frog's lymph hearts depend on the presence of electrolytes in balanced proportions, for contractions will not take place in solutions of non-conductors after the salts contained in the serum have been washed out. Contractions take place in a pure sodium chloride solution, but continue longer if a definite proportion of calcium chloride, or of some SO_4 compound, is added to the solution. A heart which has been exhausted in sodium chloride may be revived if a small amount of the salt of a bivalent ion is added to the solution. W. D. H.

Oxydase in Cerebro-spinal Fluid. By E. CAVAZZANI (*Chem. Centr.*, 1901, i, 333; from *Cent. Physiol.*, 14, 473—476).—Cerebro-spinal fluid from dogs and calves gives, after the addition of pyrogallol and sulphuric acid, a crystalline deposit of purpurogallin. The fluid gives with tannic acid a brown, with quinol a rose coloration, and with *o*-toluidine a rose-violet precipitate soluble in ether. From these observations, the existence of an oxidising ferment (cerebro-spinase) is inferred.

W. D. H.

Silicic Acid in Human and Animal Tissues. By HUGO SCHULZ (*Pflüger's Archiv*, 1901, 84, 67—100).—A number of analyses are given which show that silicic acid is found in all forms of connective tissue. Its diminution in diseased conditions has some therapeutic interest.

W. D. H.

Nature of the Sugar Present in Blood, Urine, and Muscle. By FREDERICK W. PAVY and R. L. SIAU (*J. Physiol.*, 1901, 26, 282—290).—The reducing action of the sugar obtained from blood, urine, and muscle is invariably increased after the action on it of sulphuric acid. It cannot therefore be simply glucose. This conclusion is confirmed by an examination of the osazones obtainable; mixed with glucosazone,

is a variable amount of another osazone which melts at 153—155°. The sugar from which this is derived appears to be *isomaltose*.

W. D. H.

Quantity of Sugar formed in the Animal Organism after Feeding with Various Proteids. By ERNST BENDIX (*Chem. Centr.*, 1901, i, 468—469; from *Arch. Anat. Phys.*, 1900, *Suppl.*, 309—311).—In order to determine how much sugar is formed when certain proteids are used as food, dogs were rendered free from glycogen by depriving them of exercise and excluding all carbohydrates and most proteids from their diet. They were then fed with various proteids, and at the end of half an hour were injected with phloridzin and again when 4 or 5 hours had expired; by this means, the sugar formed in the organism passes at once into the urine. The ratio of the quantity of sugar in the urine to the nitrogen present gives a measure of the amount of sugar formed by the decomposition of the proteid. Casein was found to yield more sugar than ovalbumin, although the former does not form sugar when decomposed by acids, whilst the latter yields it abundantly, and similarly, after feeding with gelatin, the urine contained less sugar than when casein was used. The leucine formed by the decomposition of the albumin in the body is converted into sugar.

E. W. W.

Glycogen in Parasitic Worms. By ERNST WEINLAND (*Zeit. Biol.*, 1901, 41, 69—74).—The amount of glycogen in certain parasitic worms is extraordinarily high, comprising, in *Taenia*, 15 to 47, and in *Ascaris* 20—34 per cent. of the dry substance. On hydrolysis, dextrose is obtained.

W. D. H.

Meat Extract. By JUNG (*Chem. Zeit.*, 1901, 25, 2—3).—The fact that Liebig's meat extract does not readily gelatinise, does not indicate that there is little or no gelatin or its hydrolytic products, gelatoses and glutinpeptone, present, since the presence of other substances, such as mineral salts and organic compounds, influences the ease with which a gelatin solution sets.

Gelatin gives Millon's reaction (compare Mörner, *Abstr.*, 1900, i, 128).

The presence of appreciable amounts of albumoses in meat extract is disproved; the total amount of albumose, albumin, and unaltered gelatin is not more than 0.94 per cent.

J. J. S.

Curdling by Rennet. By J. J. OTT DE VRIES and F. W. J. BOEKHOUT (*Landw. Versuchs-Stat.*, 1901, 55, 221—239. Compare Söldner, *Abstr.*, 1889, 634).—The authors criticise Söldner's results and conclusions, and from results obtained with milk which will not curdle, draw the conclusion that soluble calcium salts cannot have the importance which Söldner ascribes to them. Practically no calcium is rendered insoluble when milk is boiled. Addition of soluble calcium salts introduces complications, as some of the calcium enters into combination, and the acidity of the milk is increased. Söldner's view that the favourable effect of acidity on curdling is due to calcium being dissolved is incorrect. When the carbon dioxide is removed from boiled milk, previously saturated with the gas, the amount of soluble calcium

salts remains constant, but the milk becomes incapable of being curdled.

N. H. J. M.

Composition and Action of Orchitic Extracts. By WALTER E. DIXON (*J. Physiol.*, 1901, 26, 244—273).—Extracts of testis made with physiological saline solution contain (1) proteid, mainly nucleo-proteid, (2) organic substances unaltered by boiling, and (3) inorganic salts present in the dried ram's testis to the extent of 7·5 per cent. The physiological effects of injecting the extract are mainly due to the organic materials. The blood pressure falls after a somewhat lengthy latent period, and is chiefly produced by cardiac inhibition; the respiration ceases during inhibition of the heart; recovery is gradual. There is dilatation of the splanchnic, splenic, and testicular blood vessels, but constriction of the kidney vessels; this effect is probably due to action on the vaso-motor centre. Both cardiac and respiratory effects are abolished by sections of the vagus-nerves, and are probably produced reflexly. Hypoleucocytosis followed by hyperleucocytosis is another effect. These effects are mainly due to nucleo-proteid, but intravascular clotting was not observed. The substances not altered by boiling are leucomaines allied to choline, and spermine is also present; these appear to be chiefly derived from the metabolism of the glandular epithelium of the testicular ducts.

W. D. H.

Substances which Lower Blood-pressure in Suprarenal Extracts. By REID HUNT (*Proc. Amer. Physiol. Soc.*, 1900, vi—vii).—Choline is present in extracts of suprarenal glands, but there appears to be something else as well that lowers blood pressure. This second substance lowers blood pressure after the administration of atropine. On treatment of extracts with certain reagents, the amount of choline increases. This parent substance of choline is not lecithin or jecorin, but is possibly a choline ester. Similar results were obtained with brain extracts.

W. D. H.

Intravenous Injection of Minimal Doses of Epinephrine Sulphate. By REID HUNT (*Proc. Amer. Physiol. Soc.*, 1900, vii—viii).—Such small doses as 0·083 millionth of a gram of Abel's epinephrine sulphate will produce a rise of blood-pressure. It is thus many times more powerful physiologically than crude aqueous extracts of suprarenal.

W. D. H.

Excretion of Kynurenic Acid. By LAFAYETTE B. MENDEL and E. C. SCHNEIDER (*Proc. Amer. Physiol. Soc.*, 1900, ix—x).—The experiments recorded confirm the work of Mendel and Jackson, that kynurenic acid is not the result of intestinal putrefaction, but of proteid metabolism. It occurs in dog's urine after a six days' fast, and a large dose of calomel, and at a time when no ethereal sulphates are present. Feeding with gelatin, elastin, ovo-mucoid, chondrin, and thymus powder does not, however, produce an output of the acid.

W. D. H.

Oxidation Relationships of Urine Components. By ADOLF JOLLES (*Chem. Centr.*, 1901, i, 467—468; from *Ber. klin. Woch.*, 37, No. 51).—When barium chloride is added to acidified or to neutral

urine, the precipitate in both cases contains organic compounds. The quantity of potassium permanganate which is reduced by these precipitates has been determined. The precipitate obtained from the urine of healthy persons was found to require 0.198—0.243 gram of oxygen per litre, whilst that formed after acidifying the urine only required 0.079—0.096, that is, the former quantity is usually 2 to 3 times as great as the latter. In a number of diseases, the oxygen used to oxidise the precipitate from the neutral solution rose to 0.325 gram whilst that required for the precipitate from the acid solution varied from 0.052 to 0.170 gram.

E. W. W.

Ehrlich's Dimethylaminobenzaldehyde Reaction. By FR. PRÖSCHER (*Zeit. physiol. Chem.*, 1901, 31, 520—526).—The constituent of urine which gives the red coloration with dimethylaminobenzaldehyde is not one of the compounds which have so far been isolated, and is contained in larger quantity in the urine of patients suffering from typhus, phthisis, and chronic enteric fever. The red compound has the composition $C_{16}H_{24}O_6N_2$; it forms a dust-red powder soluble in alcohol, chloroform, acetic acid, epichlorohydrin, or dichlorohydrin. It also dissolves in alkalis and yields an amorphous brown precipitate with alcoholic picric acid. The constituent of urine which gives rise to the red compound probably has the composition $C_7H_{15}O_6N$.

J. J. S.

Chemistry of Nerve Degeneration. By WILLIAM D. HALLIBURTON and FREDERICK W. MOTT (*Proc. Physiol. Soc.*, 1901, xxv—xxvi).—In the disease general paralysis of the insane, the marked degeneration that occurs in the brain is accompanied by the passing of the products of degeneration into the cerebro-spinal fluid. Of these, nucleo-proteid and choline can be most readily detected. Choline can also be found in the blood. This is not peculiar to the disease just mentioned, but in various other degenerative nervous diseases (combined sclerosis, disseminated sclerosis, alcoholic neuritis, beri-beri) choline can also be detected in the blood. The tests employed to detect choline are mainly two: (1) the obtaining of the characteristic octahedral crystals of the platinichloride from the alcoholic extract of the blood; (2) the lowering of blood-pressure (partly cardiac in origin, and partly due to dilatation of peripheral vessels) which a saline solution of the residue of the alcoholic extract produces: this fall is abolished, or even replaced by a rise of arterial pressure, if the animal has been atropinised. It is possible that such tests may be of diagnostic value in the distinction between organic and so-called functional diseases of the nervous system. The chemical test can frequently be obtained with 10 c.c. of blood.

A similar condition was produced artificially in cats, by a division of both sciatic nerves, and is most marked in those animals in which the degenerative process is at its height as tested histologically by the Marchi reaction. A chemical analysis of the nerves themselves was also made. A series of cats was taken, both sciatic nerves divided, and the animals subsequently killed at intervals varying from 1 to 106 days. The nerves remain practically normal as long as they remain irritable, that is up to 3 days after the operation. They then

show a progressive increase in the percentage of water, and a progressive decrease in the percentage of phosphorus. The phosphorised fat entirely disappears when degeneration is complete. When regeneration occurs, the nerves return approximately to their previous chemical condition. The chemical explanation of the Marchi reaction appears to be the replacement of phosphorised by non-phosphorised fat. When the Marchi reaction disappears in the later stages of degeneration, the non-phosphorised fat has been absorbed. This absorption occurs earlier in the peripheral nerves than in the central nervous system.

This confirms previous observations on the spinal cord in which unilateral degeneration of the pyramidal tract by brain lesions produced an increase of water and a diminution of phosphorus in the degenerated side of the cord, which was stained by the Marchi reaction.

The Marchi reaction (the black staining produced by a mixture of Müller's fluid and osmic acid) is given by ordinary fat as contained in adipose tissue.

W. D. H.

Physiological and Toxicological Effects of Tellurium Compounds. By L. D. MEAD and WILLIAM J. GIES (*Amer. J. Physiol.*, 1901, 5, 104—149).—Non-toxic doses of tellurium (as oxide, tellurite, tartrate, and tellurate) do not materially affect metabolism in dogs. They appear to stimulate katabolism, and diminish fat absorption slightly; the urine is rendered dark brown. Large doses retard digestion, and induce vomiting and somnolence. They cause enteritis. Subcutaneously injected, they cause diarrhoea, tremors, and death from asphyxia. At the point of injection, tellurium is deposited in the metallic form, and is distributed in most of the organs and tissues. Methyl telluride appears in the breath a few minutes after the introduction of quite small amounts of tellurium into the system. It persists for months, slowly leaving the body, by skin, lungs, urine, bile, and faeces. Of the digestive ferments, trypsin is the least resistive to the destructive influence of the metal. Albumin and bile pigment are usually present in the urine.

W. D. H.

Increase of Proteid Decomposition by Protoplasmic Poisons, especially Chloroform Water in Herbivora. By OTTO ROSTOSKI (*Zeit. physiol. Chem.*, 1901, 31, 432—445).—When given in large doses, protoplasmic poisons like chloroform water cause in herbivorous, as in carnivorous, animals an increase of nitrogen output. This lasts for some days. Sometimes a preliminary fall in the excretion of nitrogen occurs. The increase of nitrogen is due to increase of urea. In rabbits, the amount of sulphur in the urine depends in great measure on the food.

W. D. H.

Behaviour of *d*-Gluconic Acid in the Organism. By PAUL MAYER (*Ber.*, 1901, 34, 492—494).—Rabbits oxidise sodium gluconate completely when it is administered to them internally. On the other hand, when this salt, or the free acid, is injected subcutaneously, part of it is oxidised to *d*-saccharic acid, which appears in the urine of the rabbits.

C. F. B.

Chemistry of Vegetable Physiology and Agriculture.

Physics of Fermentation. By EUGEN PRIOR and H. SCHULZE (*Zeit. angew. Chem.*, 1901, 14, 208—215).—Quantitative experiments on the fermentation of mixtures of dextrose and lævulose, and of maltose and dextrose by yeast cells, are described. These support the authors' views that the process of fermentation takes place inside the yeast cell, that it is dependent on the diffusion of the sugar solution through the cell wall, that the rate of diffusion through the cell wall varies for different species of yeast cells, and that in a mixture of sugars the amount of each which is fermented by yeast cells varies with the osmotic pressure of each sugar. R. H. P.

Influence of Carbon Dioxide on Fermentation [of Sucrose]. By HUGO ORTLOFF (*Centr. Bakt. Par.*, 1900, [ii], 6, 676—682, 721—733, and 753—763).—The influence of the presence of an excess of carbon dioxide has been investigated with the following results. (1) It increases the inverting power of some species of yeast, but decreases that of others. (2) It hinders the fermentation of dextrose. (3) It decreases the yield of alcohol, not only absolutely, but also relatively to the amount of sucrose fermented. (4) It has no influence on the formation of acids. (5) It decreases the "energy of multiplication," as measured by the number of cells after four days' fermentation. (6) It decreases the "power of multiplication," as measured by the number of cells at the end of the fermentation. (7) It diminishes the "energy of fermentation," as measured by the quantity of sucrose fermented in four days. (8) It, however, considerably increases the "fermenting power" as measured by the quantity of sucrose fermented in 28 days by one million cells.

Single cells produce more alcohol and more acid, when fermentation takes place in the presence of an excess of carbon dioxide than under ordinary conditions. The net result is that the fermentation is decreased, but the fermenting power increased, by the presence of an excess of carbon dioxide. R. H. P.

Enzymes. By W. ISSAEW (*Chem. Centr.*, 1901, i, 405; from *Zeit. ges. Brauw.*, 23, 796—799).—I. Malt glycase.—The most favourable temperature for the formation of dextrose in mashing is 52—60°. Malt dried at the temperature of the air yielded 2.25, light malt 1.71, and dark malt 1.30 grams of dextrose per 100 c.c. of extract, prepared by treating 100 grams of malt with 400 c.c. of water for 4 hours. The dextrose must be formed by the fermenting action of insoluble portions of the malt; even if a soluble enzyme is present, it can only play a very small part in the process.

II. Invertin.—Solutions of invertin prepared by extracting more or less plasmolysed yeast with water by Lintner's method (*Abstr.*, 1900, ii, 296) are quite as active as extracts obtained from the dried

yeast. The solubility of the invertin is not increased by adding more than 10—15 per cent. of sucrose, although the extract then contains a larger amount of substances which are coagulated on heating. By prolonging the process of plasmolysis and fermentation beyond 24 hours, the speed of inversion is affected, but the limit attained is the same. The solution obtained by extracting for 6 days at 36°, or by treating the fresh yeast with water for 24 hours, is weaker than that prepared from the yeast by 24 hours' plasmolysis followed by 24 hours' fermentation. Top fermenting yeasts contain much less invertin than bottom yeasts.

E. W. W.

Fermentation Experiments with various Yeasts and Sugars. By PAUL LINDNER (*Chem. Centr.*, 1901, i, 404; from *Woch. Brau.*, 1900, 17, 762—765. Compare this vol., ii, 182).—The action of bottom yeasts on inulin, dextrin, trehalose, melibiose, and α - and β -methylglucosides has also been investigated. Dextrin was only strongly fermented by one yeast; trehalose and α -methylglucoside gave very varying results. Inulin was decomposed by all the yeasts except two, whilst β -methylglucoside was not attacked by any. Except in a few doubtful cases, melibiose was fermented by all the yeasts. A solution of melibiose does not, however, afford a trustworthy means of distinguishing between top and bottom yeasts.

A group of wild yeasts obtained from breweries which used bottom fermenting yeasts gave the following results. Dextrin was attacked by some, but not by others, whilst raffinose was fermented by all the yeasts which fermented melibiose, but only moderately or slightly by the rest. In the case of α -methylglucoside, three yeasts gave doubtful results, and with two others there was no action. Inulin was slightly fermented by four yeasts, but generally remained intact. Trehalose was rather strongly attacked by most of the yeasts, but doubtful results were obtained with two, and in three cases it was not affected. Generally speaking, the sugars were not attacked by torula and red yeasts, but dextrose and lævulose were decomposed by two kinds.

The mixture of *l*-sorbose and *d*-galactose referred to in the previous paper (*loc. cit.*), proved to be *l*-sorbose prepared from *d*-galactose, and the ψ -tagatose was also found to be *l*-sorbose.

E. W. W.

Intracellular Nutrition of Yeast. By E. KAYSER (*Ann. Inst. Pasteur*, 1900, 14, 605—631).—The acidity produced in fermentation by yeast and caused by volatile and fixed acids is dependent on the nature of the medium and the conditions of the fermentation. The presence of acetic acid or peptone decreases the amount of fixed acids, but both fixed and volatile acids are increased in quantity by the presence of phosphates. The amount of aeration also has an effect on the relative quantity of fixed and volatile acids formed in the fermentation.

R. H. P.

Occurrence and Disappearance of Glycogen in Yeast Cells. By RICHARD MEISSNER (*Centr. Bakt. Par.*, 1900, [ii], 6, 517—525, 545—554).—The fermentation of sugar by yeast cells is accompanied by the disappearance of glycogen from the cells. The cells contain the glycogen in largest quantity when the fermenting liquid contains

about 5.5 per cent. of alcohol; the glycogen then disappears with more or less rapidity, according to the species of yeast used. Glycogen first appears in the young cells when they have attained a diameter about one-fifth of that of the parent cell. The glycogen appears to be decomposed and reformed as soon as fermentation begins; when the yeast experiences a want of sugar, the formation of glycogen ceases. Thus glycogen can be looked on as a "transitory reserve material."

R. H. P.

Experiments with Bacteria decomposing Carbamide, with the object of the Accumulation of one Variety. Decomposition of Carbamide by Urease, and by Katabolism. By MARTINUS W. BEYERINCK (*Centr. Bakt. Par.*, 1901, [ii], 7, 33—61).—The object of the investigations here described was to accumulate that variety of bacteria in a mixture, which was best adapted to the conditions of the experiment. In some cases, the experiments only resulted in the relative increase of one variety, whilst in others one variety accumulated, and the rest completely disappeared. Bacteria which decompose carbamide are of two kinds, of which one kind brings about the decomposition by means of *urease*, an enzyme insoluble in water, and the other (some phosphorescent species) by direct contact with the living protoplasm, a process which the author terms "katabolism." These two methods of decomposing carbamide are distinguished by the temperature at which the maximum decomposition takes place, the katabolic decomposition being at its maximum at the most favourable temperature for the growth of the micro-organisms, whilst the decomposition produced by urease is at its maximum at a much higher temperature.

R. H. P.

Behaviour of Denitrifying Bacteria in Culture Solutions. By ALBERT STUTZER (*Centr. Bakt. Par.*, 1901, [ii], 7, 81—88. Compare Abstr., 1900, ii, 494).—A confirmation of Jensen's results (Abstr., 1900, ii, 232, 495) and a continuation of the author's work (see Abstr., 1900, ii, 97, 359).

R. H. P.

Bacteria producing Lactic Acid and their Importance in the Ripening of Cheese. By ROBERT CHODAT and N. O. HOFMAN-BANG (*Ann. Inst. Pasteur*, 1901, 15, 36—48).—The action was investigated on casein of tyrothrix and of bacteria, isolated from Emmenthaler cheese, which produce lactic acid. The bacteria did not decompose the casein, even after it had been partly dissolved by the tyrothrix. This result is not in accordance with the views of Freudenreich, who holds that the bacteria which produce lactic acid play the greater part in the ripening of cheese (Abstr., 1900, i, 712); compare also Epstein, this vol., ii, 119).

R. H. P.

Bacillus Carotovorus, the Cause of a White Rot of Carrots. By LEWIS RALPH JONES (*Centr. Bakt. Par.*, 1901, [ii], 7, 12—21, and 61—68).—The organism which causes the rotting of carrots is not the same as that which affects turnips. *Bacillus carotovorus* is motile, does form spores, liquefies gelatin, produces at first an acid but after-

wards an alkaline reaction in meat broth, curdles milk, is a facultative anaerobe, and will convert nitrates into nitrites. R. H. P.

Modification of the Functions of *Bacillus Coli*. By LÉON GRIMBERT and G. LEGROS (*J. Pharm.*, 1901, [vi], 13, 107—109).—Attempts made to deprive *Bacillus coli* of its characteristic functions, by cultivation under various abnormal conditions, resulted in two only out of five different types being deprived of their power to produce indole, whilst in no case was their power to ferment lactose destroyed. H. R. LE S.

Reduction of Sulphates in Brackish Water by Bacteria. By R. H. SALTET [and C. S. STOCKVIS] (*Centr. Bakt. Far.*, 1900, [ii], 6, 648—651, 695—703. Compare Beyerinck, this vol., ii, 120).—The reduction of sulphates to hydrogen sulphide in brackish water takes place in at least two stages: the sulphates are partially reduced to sulphites or other oxygenated sulphur compounds by *Bacillus desulfuricans* and these are afterwards reduced to hydrogen sulphide by other species of bacteria. R. H. P.

Biology and Chemistry of Diphtheria Bacilli. By HANS ARONSON (*Chem. Centr.*, 1901, i, 471—472; from *Arth. Kinderheilkunde*, 30).—When diphtheria bacilli from which the fat has been removed by ether and alcohol are treated with dilute sodium hydroxide solution by H. Kossel's method, the solution obtained contains only a small quantity of the poisonous substance, and thus differs entirely from the extract prepared by means of a 0.1 per cent solution of ethylene-diamine. Since the solution of the toxin is little affected by treating with alcohol and ether, it cannot be an albumin. The precipitate formed when acetic acid is added to the filtrate contains a large quantity of the poisonous substance. By treating the bacilli freed from fat with a dilute solution of alkali, first at the ordinary temperature, then at 100°, and finally under pressure at 130°, extracts are obtained from which acetic acid precipitates substances which give the reactions of albumin. The white powder prepared by repeated purification of the precipitates is not separated from its solutions in alkalis by acetic acid and is a nucleic acid corresponding with Ruppel's tuberculinic acid (*Abstr.*, 1899, ii, 237) but is not identical with it. By heating with hydrochloric acid the substance obtained by means of acetic acid, xanthine bases and pentoses are formed, hence it not only contains albumin but also nucleoproteids. No characteristic toxin could be detected in the diphtheria bacilli. The fat extracted from the bacilli is very deliquescent. The mass left after completely extracting the bacilli with alkali contains a carbohydrate which almost completely dissolves on boiling with a 1 per cent. solution of hydrochloric acid; the filtrate reduces Fehling's solution, is dextrorotatory, and yields an osazone. This carbohydrate is neither cellulose nor chitin. E. W. W.

Morphology of the Organisms Designated "*Bacterium Radicicola*." By ALBERT STUTZER (*Bied. Centr.*, 1901, 30, 60—63; from *Mitt. Landw. Inst. k. Univ. Breslau*, 1900; *Heft*, 3, 57).—Extracts of green leguminous leaves, with or without addition of agar,

are very suitable for cultivating *Bacterium radicum*, but all attempts to obtain the branched forms failed when neutral or slightly alkaline media were employed.

Later experiments in which small amounts of organic acids (0.05 per cent.) were added to the solutions previously employed showed a production of the branched forms. Potassium phosphate is a necessary constituent, and magnesium sulphate favours the production of good forms of growth: sodium, calcium, and iron, &c., are without influence, Dextrose (1 per cent.) is favourable, as are also inulin and starch meal, whilst gum arabic, sucrose, lævulose, molasses, and lactose are less favourable. Peptone alone was found to be equal to asparagine, and is perhaps more favourable to the production of branched forms than asparagine. The frequent use of fresh acid solutions increases the number of branched forms.

Branching also takes place in solutions containing dextrose, asparagine, magnesium sulphate, and potassium dihydrogen and dipotassium hydrogen phosphates (but without organic acid). The best results were obtained when the solution contained potassium dihydrogen phosphate (1 per thousand) or the monopotassium salt, 0.75, and dipotassium salt, 0.25 per thousand.

N. H. J. M.

Formation of Solanine in Potatoes as a Product of Bacterial Action. By RICHARD WEIL (*Arch. Hygiene*, 1900, 38, 330—349).—Some potatoes were found to contain as much as 0.38 per cent. of solanine. From the grey spots on these, and the portions of the potato immediately surrounding them, thirteen species of bacteria were isolated; of these, two, *Bacterium solaniferum non colorabile* and *B. solaniferum colorabile* cause the formation of solanine when cultivated on potatoes.

R. H. P.

Chemistry of Bacteria. By ERNST BENDIX (*Chem. Centr.*, 1901, i, 406—407; from *Deutsch. med. Woch.*, 27, 18—19).—A pentose has been obtained from tuberculosis bacilli by boiling the dried bacilli with a 5 per cent. solution of hydrochloric acid. The solution reduced alkaline copper solutions, gave the characteristic orcinol hydrochloric acid reaction and with phenylhydrazine formed an osazone which melted at 153—155°. The pentose was found to be contained in the nucleo-proteids of the bacilli. A mixture of faecal bacteria cultivated in urine and the bacilli of diphtheria both showed the pentose reactions, but the bacilli of typhus gave negative results.

E. W. W.

Germination in Distilled Water. By PIERRE DEHÉRAIN and DEMOUSSY (*Compt. rend.*, 1901, 132, 523—527. Compare Boehm, *Ann. Agron.*, 1875, i, 470; DehéRAIN, *ibid.*, 1878, 4, 321, and DehéRAIN and Bréal, *ibid.*, 1883, 9, 58).—Germinating seeds form roots, and begin their evolution, in water quite free from calcium, but the development of roots in distilled water is checked by very slight traces of copper (compare Coupin, *Abstr.*, 1899, ii, 118). Fungi, algæ, and germinating vegetable seeds show the presence of traces of a metal, such as copper, which cannot be detected by means of the reactions usually employed.

N. H. J. M.

Behaviour of the Pentosans of Seeds during Germination. By A. SCHÖNE and BERNHARD TOLLENS (*Chem. Centr.*, 1901, i, 467; from *Diss.*, 1899, *Rostock*).—The percentage of pentosans contained in barley, wheat, and peas was found to be greater after germination than before, and a slight increase in the total quantity was also observed in each case. The new pentosans are probably derived from the starch, and the pentosans cannot therefore be regarded as reserve nutritive material which disappears during respiration. E. W. W.

Physiological Function of Enzymes in Vegetable Life. By MARCO SOAVE (*Bied. Centr.*, 1901, 30, 29—32; from *Staz. Sper. Agrar. Ital.*, 1899, 32, 553).—In experiments with seeds of *Arachis hypogaea*, it was found that chloroform and ether hindered germination, but did not kill the seedlings. In the case of ether, the chemical changes were scarcely affected. N. H. J. M.

Composition of the Cocoa-nut during Germination. By J. E. KIRKWOOD and WILLIAM J. GIES, (*Proc. Amer. Physiol. Soc.*, 1900, xiv—xv).—A tabular statement, giving water, solids, ash, and nitrogen in different parts of the cocoa-nut at various stages of its growth. The cotyledon, especially the central nerve vascular portion, contains a considerable amount of diastatic ferment, and a trace of proteolytic enzyme. Enzymes which dissolve cellulose and hydrolyse fats were not found. W. D. H.

Assimilation of Carbon Dioxide by Hyphomicrobium and Nitromicrobium. By ALBERT STUTZER (*Bied. Centr.*, 1901, 30, 58—60; from *Mitt. Landw. Inst. K. Univ. Breslau*, 1900, Heft 3, 36).—In inorganic solutions, hyphomicrobium only developed satisfactorily in presence of free carbon dioxide; addition of mannitol or sodium lactate did not affect the result.

Similar results were obtained with nitromicrobium; mannitol had no effect. N. H. J. M.

Influence of Pressure on Chlorophyllous Assimilation. By JEAN FRIEDEL (*Compt. rend.*, 1901, 132, 353—355. Compare Abstr., 1900, ii, 679).—The diminution of the total pressure alone tends to further assimilation. The isolated action of the pressure of carbon dioxide, and the isolated action of the total pressure, are both modified, and in a different manner, by the amount of carbon dioxide present in the air. These modifications are, however, such that the resulting phenomenon follows the same law within fairly wide limits. When air containing carbon dioxide is simply rarefied, assimilation is first reduced to a minimum and then increases to a maximum.

N. H. J. M.

Reserve Carbohydrate in the Root Swellings of Arrhenatherum bulbosum. By V. HARLAY (*Compt. rend.*, 1901, 132, 423—426).—In preparing the carbohydrate, methods similar to those described by Ekstrand and Johanson (Abstr., 1888, 246 and 439), by Müntz, and by Bourquelot and Hérissé (Abstr., 1900, ii, 301, and *J. Pharm.*,

1900, [vi], 11, 589) were employed. The substance very much resembles phléin and graminin (Ekstrand and Johanson, *loc. cit.*), its melting point (212°) and rotatory power ($\alpha_D - 44.7^{\circ}$) being between those of the latter carbohydrates; it also differs from inulin by its greater solubility.

The carbohydrate, which the author also terms graminin, is not altered by saliva or by diastase, but was partially (one-twelfth) converted into sugar by 20 hours' contact with the ferments secreted by *Aspergillus niger*. The same result was obtained by the action of the root sap of *Arrhenatherum bulbosum*, whilst the sap from the green portions of the plants had no action.

The fresh root swellings contain 7.5 per cent. of graminin; lævulose, and perhaps dextrose, also seem to be present. N. H. J. M.

Catha edulis. By ALBERT BEITTER (*Arch. Pharm.*, 1901, 239, 17—33).—*Catha edulis* is a shrub which is cultivated in Abyssinia and Arabia, and is consumed largely by the inhabitants of those regions, being either chewed or taken as an infusion. It acts as a stimulant, inducing wakefulness at the same time; its use in Eastern Africa is on a level with that of tea, coffee, and alcohol in Europe.

The leaves were extracted with chloroform containing ammonia, the extract was evaporated, and the residue extracted with very dilute hydrochloric acid. From the acid extract, a crystalline *alkaloid* was separated with great difficulty, but the amount obtained was so small that no satisfactory analysis could be made. The composition, however, corresponds approximately with that required by the formula $C_{10}H_{18}ON_2$; the basic character of the alkaloid is fairly pronounced, and crystalline salts, namely, *acetate*, *sulphate*, *hydrochloride*, *hydrobromide*, and *salicylate*, were prepared, although not analysed. The residue, after extraction of the alkaloid with acid, was purified by dissolving it repeatedly in chloroform and precipitating it with alcohol; it has approximately the composition $C_{10}H_{17}O$, is completely melted at 120° , and has the properties of caoutchouc. By extracting the leaves, already exhausted with chloroform, with water, and precipitating with lead acetate, a *tannin* is obtained very similar to that of tea. The filtrate from the lead precipitate was found to yield mannitol, the presence of which was suspected by Schorlemmer (*Chem. News*, 1883, 48, 225). By distilling the chopped leaves with superheated steam, a very small quantity of an *essential oil* is obtained, probably containing oxygen. The seeds contain 51 per cent. of a *fatty oil* which consists of the glycerides of fatty acids, and has the Hübl number 103.9. The ash contains magnesium, calcium, and iron, combined with chlorine and carbonic, sulphuric, and a trace of sulphurous acids. C. F. B.

Large yield of Manna by Olive Trees. By J. A. BATTANDIER (*J. Pharm.*, 1901, [vi], 13, 177—179).—Details of the chemical examination of manna, a summary of which has already appeared (Trabut, this vol., ii, 184). H. R. LE S.

Chemistry of Rhubarb. By CARL G. HUNKEL (*Pharm. Arch.*, 1900, 3, 201—216).—A *phenolic* substance, $C_{10}H_{10}O_4$ or $C_{12}H_{11}O_5$, was

obtained, softening at 172—173° when heated, and unstable in character. Sucrose was isolated in a crystalline state, and some evidence of the presence of dextrose was obtained. In other respects, the results obtained do not seem to add much to what was known already. C. F. B.

Manufacture of Wine. IV. Soluble Constituents of Vine Leaves. By CARL BOETTINGER (*Chem. Zeit.*, 1901, 25, 6—8, 17—18, 24—25).—The aqueous extract of vine leaves gathered at the end of July contains calcium and potassium hydrogen tartrates, and alkali phosphates, together with a small amount of a sugar which may be isolated in the form of an osazone melting at 205—206°.

The alcoholic extract contains tartaric, succinic, and pyrocatechuic acids, together with other products not yet identified. J. J. S.

Water Chesnut (*Trapa natans*, L.). By ALEXANDER ZEGA and DOBR. KNEZ-MILOJKOVIĆ (*Chem. Zeit.*, 1901, 25, 45. Compare Neumann, *Abstr.*, 1899, ii, 794).—The following are the results of analysis of I, the kernel; and II, the shell:

| | Water. | N com- pounds. | Fat. | Carbo- hydrates. | Woody tissue. | Ash. | P ₂ O ₅ . |
|-----|--------|-------------------|------|---------------------|------------------|------|---------------------------------|
| I. | 37·19 | 10·34 | 0·71 | 48·99 | 1·36 | 1·41 | — |
| II. | 39·71 | 8·04 | 0·80 | 48·94 | 1·27 | 1·24 | 0·56 |

The nut is largely used as a food, both green and ripe. In the uncooked state, it tastes somewhat like the chesnut. J. J. S.

Mercurial Poisoning of Green Plants. By FRANZ W. DAFERT (*Chem. Centr.*, 1901, ii, 331—332; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 4, 1—9).—By placing the plants in a bell-jar standing over mercury, it has been found that barley, wheat, rye, oats, red clover, *Picea vulgaris*, *Aster chinensis*, *Sinapis alba*, and *Verbena officinalis* are all sensitive to the action of a very small quantity of mercury vapour, which prevents growth and causes the death of the portions of the plant which contain chlorophyll. In most cases, there are no characteristic symptoms of poisoning, but when the air enters through a very small mercury valve, such symptoms are exhibited under certain conditions. The young plants are more easily affected than the older ones, and mustard and barley are the most quickly attacked. In the case of plants which are affected by the moisture in the air, the poisonous action is most marked when the air is the most humid.

When the mercury is covered with a layer of glycerol, the plants remain without injury. E. W. W.

[Pot Experiments on the Action of Sodium Iodide and Bromide, and Lithium Chloride on Crops.] By J. AUGUSTUS VOELCKER (*J. Roy. Agr. Soc. Engl.*, 1900, [iii], 11, 566—591).—The object of the experiments was to ascertain the effect of the rarer ash constituents of plants when applied as manures. The present report contains the results obtained in 1898 and 1899.

Sodium iodide, at the rate of 200 cwt. per acre, killed wheat, barley, and red clover; peas were slightly benefited. When applied at the rate

of 1 cwt. per acre, sodium iodide injured both wheat and barley. A top dressing of $\frac{1}{2}$ cwt. was injurious to wheat and barley. Soaking the seeds in 1 per cent. iodide solution increased the yield of wheat and barley, grain and straw, and benefited the red clover.

Sodium bromide, 100 or 200 cwt. per acre, or $\frac{1}{2}$ cwt. top-dressed, very greatly reduced the yield of wheat, but the effects on barley were not so marked. The effects of 200 cwt. or smaller amounts, on red clover were injurious rather than beneficial. Soaking seeds with 1 per cent. of sodium bromide was more or less beneficial in each case. Lithium chloride (500 cwt.) at first retarded the growth of wheat, which, however, subsequently grew fairly well; the effect on barley was similar, whilst mustard failed and peas germinated badly. Smaller amounts (200 cwt.) slightly benefited peas. Sodium iodide and bromide rendered the soil impervious, and the iodide pots gave off an odour of iodine.

A water-culture experiment is described in which wheat was grown without and with sodium iodide ($I=1:43,700$); photographs of the roots show that those of the plants grown under the influence of iodide were quite dwarfed. The total air-dried plants weighed 0.277 gram without, and 0.141 gram with, sodium iodide.

N. H. J. M.

[Pot Experiments on Wheat and Barley.] By J. AUGUSTUS VOELCKER (*J. Roy. Agr. Soc. Engl.*, 1900, [iii], 11, 594—603).—Results of comparative experiments with large and small seeds (wheat and barley) indicated that the size of the seed does not have much effect on the yield or on the weight of the seed produced. Climatic conditions at the ripening period are more probably the determining factors.

As regards the question of the production of hard or soft wheat, it was found that the sowing of either kind does not necessarily result in the production of wheat of the kind sown. Besides the character of the season at the time of ripening, it is shown that the nature of the soil is of importance. Heavy soil on which soft wheat was sown produced only hard wheat.

Ears which were at all blighted were always glutinous and never starchy. Experiments were made on the effect of different materials on "smutty" wheat. Hot water, copper sulphate, potassium sulphide, and a mixture containing copper sulphate and carbolic compounds were tried. All the applications were very beneficial, but treatment with hot water (not exceeding 133° F.) was as effectual as any.

N. H. J. M.

Use of Sodium Nitrate containing Perchlorate. By J. AUGUSTUS VOELCKER (*J. Roy. Agr. Soc. Engl.*, 1900, [iii], 11, 603).—Sodium nitrate free from perchlorate, and also a sample containing 2.15 per cent. of perchlorate, were applied at the rate of 1 cwt. per acre to barley grown in pots. The perchlorate had no injurious effect on the growth of barley, and the weight of grain and straw were equal to that obtained with pure sodium nitrate.

Difficulty was experienced in obtaining sodium nitrate containing perchlorate in appreciable quantity.

N. H. J. M.

Cultivation of Leguminous Plants. By L. MALPEAUX (*Ann. Agron.*, 1901, 27, 65—81).—Germination experiments made with

various leguminous seeds showed that addition of sodium nitrate (1·5 grams to 10 kilograms of sand) is injurious, especially in the case of lucerne and incarnate clover (compare Claudel and Crochetelle, *Abstr.*, 1896, ii, 442).

Sodium nitrate was found to be slightly beneficial when applied to young plants grown in sand, but rather retarded growth in ordinary soil except in the case of peas. Nodules are formed on the roots in a comparatively short time; they were found on lupin roots in 12 days, on haricot roots in 14 days, and on pea roots only after 22 days.

Nodules are nearly always formed on the roots of leguminous plants, the necessary bacteria being carried by wind or by birds; the absence of nodules indicates that the soil is unfavourable to the development of the bacteria.

Nitric nitrogen seems to be directly assimilated by the *Leguminosæ* and may cause complete absence of root-nodules. The conclusion is drawn that manuring with nitrate is quite useless for leguminous crops.

N. H. J. M.

Cultivation of Gorse. By HENRI GUÉPIN (*Ann. Agron.*, 1900, 27, 106—107; from *J. Agr. Prat.*, 1899, ii, 661. Compare Girard, this vol., ii, 187).—Gorse requires neither nitrogen nor lime, but is benefited by phosphates and especially by potash. The crop may be cut every year from the second year, and lasts about seven years. The yield is estimated at 30,000 to 40,000 kilos., corresponding with 15,000 kilos. of hay.

N. H. J. M.

Gorse as Food for Sheep. By J. AUGUSTUS VOELCKER (*J. Roy. Agr. Soc. Engl.* 1899, [iii], 10, 567—573).—The gorse was sown in May, 1897, between alternate rows of barley, on some very poor sandy soil at Woburn. No manure was applied. The yield of gorse cut at the end of 1898 was 11 tons per acre.

Feeding experiments with sheep were instituted to ascertain in the first place how far gorse can be employed as a substitute for roots.

It was found that 2·5 lbs. of gorse was the greatest amount consumed per day (corresponding with about 6 lbs. of roots). The gorse proved, however, to be decidedly beneficial, as regards the general health of the sheep, the increase in live weight and the quantity of the meat, and its employment as additional food is therefore recommended.

The average composition of the gorse as fed was as follows: water, 55·95; nitrogen, 0·84; ether extract, 1·17; soluble carbohydrates, digestible fibre, &c., 19·77; woody fibre, 15·04, and ash, 2·79 (including sand, 1·15 per cent.).

N. H. J. M.

Maintenance Ration of Cattle. By HENRY PRENTISS ARMSBY (*Bul. Pennsylvania State Coll. Agr. Exper. Stat.*, No. 42, pp. 188).—The experiments were made during the years 1892—1893 to 1896—1897. As regards the results relating to digestibility, it is thought that the variations observed are chiefly due to variations in the rate of excretion of the fæces.

The results of twelve experiments indicate that the maintenance food per 500 kilograms of live weight represents 12,771 Cal. at 51° F. The average of nine experiments by Kühn and Kellner computed to

the same weight 12,952 Cal. at 61° F. As a general result, the maintenance of a steer (500 kilos.), receiving mainly or exclusively coarse food, may be placed at 13,000 Cal. of available energy at a temperature of 50—60° F. after deducting energy lost by the formation of methane.

As regards the minimum of proteids, about 300 grams per day per 500 kilos. of live weight is required when the nutritive ratio is 1:11; any material diminution will result in a loss of live weight. When, however, the nutritive ratio is much wider, the amount of proteids may be reduced, at any rate for a time, without any material loss of nitrogen in the body.

N. H. J. M.

Hemp Cake. By ALFRED LEMCKE (*Landw. Versuchs-Stat.*, 1901, 55, 161—182. Compare Abstr., 1894, ii, 113, 155, 291, and 469).—In hot countries, hemp is not grown for the fibre, which is too coarse, or for the seed oil, but on account of a narcotic, resinous secretion, and a constituent which is extracted by boiling.

The average composition of hemp cake (from 661 analyses) was found to be as follows:

| Water. | Proteid. | Fat. | N-free extract and crude fibre. | Ash. |
|--------|----------|-------|------------------------------------|------|
| 10·81 | 30·76 | 10·17 | 40·59 | 7·67 |

The amounts of proteid varied from 26·85 to 33·85; the fat from 7·85 to 19·35; the ash was generally normal, but in isolated cases the percentage was as high as 10 or even 14·60. The amount of water varied from 8·30 to 22·28 per cent.

Intentional adulteration of hemp cake seldom occurs, and an abnormal composition is generally the result of imperfect methods of manufacture. Hemp cake is a good substitute for oats for horses, when the amount does not exceed 1 or 1·5 kilogram per day; larger amounts cause thirst and restlessness. Good results were obtained with cows, which received 500 grams of the cake mixed with roots and bran; large quantities cause indigestion and injure the quality of the milk. For fattening, as much as 2·5 kilograms may be given, together with sunflower or cotton cake and crushed barley.

The mean acidity of the cake was found to be 1·08 per cent. (maximum 6·07 and minimum 0·37 per cent.).

The various fungi found in hemp cake are referred to, and also the results of observations showing the number of bacteria, which is very high, per gram.

N. H. J. M.

Nitrogenous Compounds in Molasses. By C. BEGER (*Chem. Zeit.*, 1901, 25, 8—10).—Molasses contain 1·47 per cent. of nitrogen; of this nitrogen, some 5·3—12·2 per cent. is present as proteid nitrogen, 29·3 per cent. in the form of organic bases such as betaine, and 48·3 per cent. as amino-compounds such as glutamine.

Molasses is not a suitable food material for dogs, as when fed on it they lose some 12 grams in weight per day, indicating that the nitrogen compounds present cannot replace proteids.

J. J. S.

Soil Samples From German East Africa. By ALBERT STUTZER (*Bied. Centr.*, 1901, 30, 1—3; see this vol., ii, 283).

Agricultural Value of Madagascar Soils. By ACHILLE MÜNTZ and E. ROUSSEAU (*Compt. rend.*, 1901, 132, 451—456).—The littoral zone of the island is satisfactory as regards fertility. The red soils of the central portions are very poor, especially in potassium and calcium, and are not suitable either for crops or for forests; there are, however, richer soils at the bottom of the valleys. On the whole, the country is not well provided with the materials necessary for the growth of crops, and would not support a very dense population. There are several difficulties in the way of the importation and distribution of manures, but it is thought that much may be effected by irrigation. N. H. J. M.

Elimination of Methane from the Atmosphere. By V. URBAIN (*Compt. rend.*, 1901, 132, 334—336).—Atmospheric methane is constantly produced by the fermentation of cellulose, &c. [Hoppe-Seyler, *Abstr.*, 1886, 577, 932]. The results of analyses made in 1884, by Müntz and Aubin (*Abstr.*, 1885, 118), and in 1900 by Gautier, compared with Boussingault's results, show, however, no increase in the amount of methane. Volta supposed that the methane was burnt under the influence of lightning, whilst Davy, who showed that combustion cannot take place when the gas is diluted with 17 volumes of air, attributed its destruction to the action of ozone.

Experiments made by the author showed that, under the most favourable conditions, methane is only partially oxidised by ozone.

The results of vegetation experiments, extending over several months, in which enclosed plants were supplied from time to time with fresh amounts of methane, showed that considerable amounts of the gas were absorbed. The conclusion is drawn that the accumulation of methane in the air is prevented by its absorption by plants.

N. H. J. M.

Hydrolysis and Decomposition of Fats and Fatty Acids in the Soil. By MAX RUBNER (*Arch. Hygiene*, 1900, 38, 67—92).—Fats suffer little or no decomposition in sterile soil; they are, however, hydrolysed through the agency of bacteria even in dry soil. This decomposition of fats in the soil is much increased in the presence of calcium carbonate, which by interaction with the acids produced by the hydrolysis of the fats forms soaps; these with free fatty acids constitute the "wax" resulting from the decomposition of fats in the soil. R. H. P.

Calcium Compounds in Soils. Estimation of Assimilable Calcium. By D. MEYER (*Chem. Centr.*, 1901, i, 267—269; from *Landw. Jahrb.*, 29, 913—1000).—Kellner's method for determining the lime requirement of soils is modified as follows. The soil which has passed through a 2 mm. sieve (25 grams) is digested for 3 hours at 100° with 10 per cent. ammonium chloride solution (100 c.c.), diluted to 250 c.c., and filtered through a hardened filter paper (Schleicher and Schüll, No. 602). A tenth of the whole, diluted to 80—90 c.c., is slightly acidified with acetic or citric acid, boiled, and treated with ammonium oxalate in the usual manner. The total calcium should be determined in peat and calcareous soils.

The solubility of calcium in dilute hydrochloric acid varies considerably in different kinds of soils. In heavy soils, most of the

calcium is in the finest portions, whilst in light soils the coarser constituents often contain a good deal. The solubility of the magnesium generally resembles that of the calcium and the amounts of magnesium, phosphoric acid, and sulphuric acid vary, like that of calcium, in the particles of different sizes. In light soils, most of the calcium is in the form of readily decomposable silicates.

When the effect produced by pure calcium carbonate on the growth of plants = 100, that of dolomite and basalt = 99—100; basic slag, scolecite, anorthite, diabase, and nephelite = 80—90; apophyllite = 70—80; phosphorite = 60—70; calcium diphosphate and apatite = 50—60; fluor spar = 40—50; and monocalcium phosphate = 30—40. Calcium and magnesium carbonates together gave the best results, and magnesium sulphate had no favourable effect. Basic slag, among phosphates, gave the best results, then apatite and phosphorite, and lastly di- and mono-calcium phosphates. In using superphosphate, it is of importance to have a sufficient amount of lime to combine with the excess of acid. Basic slag was the only phosphate favourable to leguminous plants; zeolites were, however, especially favourable. Gypsum was injurious in pot experiments.

As a rule, the amount of calcium taken up was about proportional to the growth, but the calcium of silicates was utilised more sparingly than that of carbonates; the relations of the amounts taken up were as follows: calcium carbonate, 100; apophyllite, 69; scolecite, 51.7; and anorthite, 46.7.

The application of magnesium in conjunction with calcium carbonate lowers the percentage of calcium but considerably raises that of magnesium. No relation between the amount of calcium in the soil and the amount taken up by the plant can be shown by determining the carbon dioxide. Abundance of carbon dioxide generally indicates plenty of available calcium, but a low percentage of carbon dioxide is no certain indication of a deficiency.

The results of experiments with rye showed that application of lime had no appreciable effect on the amount of calcium in the grain, and only increased the percentage in the straw when there was no increase in the crop under the influence of lime.

Soil containing 0.25 per cent. of lime, according to the method described above, may be considered normal; but there should not be less than 0.2 per cent. It is quite immaterial whether the soil is light or heavy.

N. H. J. M.

Absorption of Monocalcium Phosphate by Arable Soil and Humus. By J. DUMONT (*Compt. rend.*, 1901, 132, 435—437).—In humous soils, the fixation is not due exclusively to retrogradation, and the amount absorbed depends on the extent of the relation of humus to calcium carbonate, and not on the amount of carbonate.

Abundance of humus distinctly reduces retrogradation.

N. H. J. M.

Influence of Manure and the amount of Water in the Soil on the Growth and Composition of Barley. By CONRAD VON SEELHORST and N. GEORGS (*Chem. Centr.*, 1901, i, 533; from *J. Landw.*, 48, 325—347).—To produce good barley, especially for brewing, nitrogenous manure must be applied in moderation, particularly when the

soil is dry. In moist soils, there is less danger of nitrogenous manure producing highly nitrogenous barley. N. H. J. M.

Effect of different forms of Phosphoric Acid. By FRANZ W. DAFERT and OTTO REITMAIR (*Chem. Centr.*, 1901, i, 231—232; from *Zeit. landw. Versuchs.-Wes. Oesterr.*, 1900, 3, 589—611).—From the results of numerous field experiments, in which attention was given chiefly to the yield of grain, whilst less importance was attached to the amount of phosphoric acid taken up and to the production of straw, the following conclusions are drawn.

Basic slag with high citrate solubility is not better than slag of low citrate solubility; the manure is to be valued according to the total phosphoric acid it contains.

Degelatinised bone meal gave good results with summer cereals, indicating that field experiments alone furnish trustworthy results as to the value of manure, since, according to the results of pot experiments, bone meal is of less value.

Algerian phosphate proved to be equal to basic slag as a manure for summer cereals. Further experiments should be made with crude phosphates on ordinary arable land.

The effect of superphosphate, calculated from the increased yield of grain, was, compared with that of basic slag, as 100 : 70 for oats, and about the same for barley.

The value of the phosphates, as indicated by the above experiments, is not immediately available for agricultural practice; the experiments must be continued for several years. N. H. J. M.

Manurial Effect of Degelatinised Bone Meal. By FRANZ W. DAFERT (*Chem. Centr.*, 1901, i, 533; from *Zeit. landw. Versuchs.-Wes. Oesterr.*, 1901, 4, 96—98).—In reference to the results obtained by Kellner and Böttcher (following abstract), indicating a relation between the effect of bone meal and the amount of calcium in the soil, attention is called to the experiment of the author and Reitmair (preceding abstract). Soils containing much calcium gave, with one exception, greatly increased yields under the influence of bone meal. Unfavourable results are therefore to be attributed to other causes, as yet unexplained. N. H. J. M.

Manurial Action of Bone Phosphoric Acid. By OSCAR KELLNER and O. BÖTTCHER (*Bied. Centr.*, 1901, 30, 7—12; from *Deut. landw. Presse*, 1900, 27, 665).—Experiments are described in which oats were grown in pots containing 6 kilograms of soil (a) without phosphatic manure, (b) with superphosphate (0.25 gram P_2O_5 , soluble in water), (c) with basic slag (0.25 gram P_2O_5 , citrate soluble), and (d, 1—10) with bone meal (containing $P_2O_5 = 0.4$ gram). Similar pots received the same manures in double quantity, and there were, in each case, two sets, one with, and the other without, calcium carbonate.

Addition of lime caused in every case a reduction in the yield, but the reduction was essentially less where superphosphate and basic slag were employed than with bone meal. In comparing the amounts of increase due to phosphoric acid applied, it is, however, seen that the

addition of lime is not unfavourable when used in conjunction with basic slag and superphosphate.

In the case of the smaller application of bone meal, addition of calcium carbonate reduced the yield on the average by 67 per cent.

On the majority of soils, the autumn application of bone meal will have a very considerable effect ; but the manure should not be applied to calcareous, or to freshly limed, soils.

N. H. J. M.

Phosphorite and Green Manure. By A. N. ENGELHARDT (*Chem. Centr.*, 1901, i, 232 ; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 1900, 3, 631—648).—Field experiments with phosphorite were made from 1886 to 1889. The soil contained very little phosphoric acid in the form of non-assimilable organic compounds. Phosphorite meal gave excellent results with cereals, especially rye, due to the non-crystalline calcium phosphate. The manure is suitable for all soils poor in available phosphates which contain sufficient nitrogen, potash, and lime, but not for soils which give good results without stable manure. When phosphorite ceases to be effective, green manuring should be tried ; other minerals, especially marl, might be of use.

N. H. J. M.

Lysimeter Experiments in 1899. By JOSEPH HANAMANN (*Chem. Centr.*, 1901, i, 270 ; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 1901, 4, 34—39. Compare Abstr., 1899, ii, 515).—Notwithstanding the heavy rainfall during the vegetative period, the drainage was more dilute than previously ; the soil having become more consolidated, the dissolved matters were more thoroughly taken up by the roots. Fallow soil lost the most, including nitrogen, then the soil bearing young red-clover plants ; the rape and bean soils lost still less, and the soils with summer cereals, which require the most nitrogen, least of all.

Calcium is the most subject to loss ; potassium and sodium are lost in about equal amounts. There were considerable losses of chlorine and sulphuric acid, greatest in fallow, and least in bean and clover soils. Traces of phosphoric acid were detected in the drainage from fallow soil, but it could scarcely be detected in the other drainage waters.

N. H. J. M.

Analytical Chemistry.

Titration of the Alkalinity of Solutions containing Hypochlorites, Chlorates and Chromates. By HERMANN VON HUBER (*Zeit. Elektrochem.*, 1901, 7, 396—398).—The chromate is first precipitated as the barium salt, and, if present in large quantities, filtered off. The hypochlorous acid and hypochlorites are then destroyed by the addition of a neutral solution of sodium sulphite or sodium thiosulphate, and the alkali titrated, using methyl-orange as indicator.

T. E.

Decomposition of Chlorides by Ignition with Organic Matter. By HERBERT E. DAVIES (*J. Soc. Chem. Ind.*, 1901, 20, 98—100).—The author has found that when chlorides are ignited with organic matter, there is a serious loss of chlorine, particularly in the earlier stages of the combustion. As may be expected, the loss is very great in the case of calcium and magnesium chlorides, but with barium chloride and even sodium chloride there is also a serious loss, not from volatilisation of the compound, but of its chlorine. The loss seems greatest when the amount of chlorides is small, and decreases when the chlorides increase in amount.

The loss may be altogether prevented by adding, before ignition, a solution of sodium carbonate equivalent to 5 per cent. by weight of the organic matter.
L. DE K.

Estimation of Sulphides, Hydrosulphides, Polysulphides, and Thiosulphates existing together in Solutions and particularly in Sulphuretted Mineral Waters. By ARMAND GAUTIER (*Compt. rend.*, 1901, 132, 518—523).—The whole of the sulphur existing in solution as free hydrogen sulphide, or one-half of this element contained in a soluble hydrosulphide, is expelled on distilling the liquid under reduced pressure, and may be precipitated as silver sulphide by passing the evolved gas into a half-saturated warm solution of silver sulphate. The soluble monosulphides are not affected by this treatment, and the sulphur in these compounds may be subsequently estimated by distilling the solution in a current of carbon dioxide under reduced pressure. Polysulphides also are decomposed by carbon dioxide, giving off an amount of hydrogen sulphide corresponding with 1 atom of sulphur to each mol. of the compound, whilst the excess of sulphur is precipitated in the free state. When these substances are present, the distillation must be carried out in a vacuum, and at temperatures below 30°, otherwise the precipitated sulphur would react with the alkali carbonate in the following manner, $4S + K_2CO_3 = K_2S_2O_3 + 2H_2S + CO_2$, and moreover the polysulphides themselves are decomposed by hot water in accordance with the equation $K_2S_5 + 3H_2O = K_2S_2O_3 + 3H_2S$.

The sulphur derived from the poly-sulphide is precipitated by adding zinc acetate and heating the solution to boiling; the precipitate is then oxidised by fuming nitric acid, and the sulphur estimated as barium sulphate.

The thiosulphates in the final filtrate are estimated iodometrically in the ordinary way.
G. T. M.

Toxicological Detection of Nitric Acid. By GUSTAVE FLEURY (*Ann. Chim. anal. appl.*, 1901, 6, 12—13).—The finely minced organs, such as the liver, are extracted with thrice their weight of very strong alcohol, and after a few hours the liquid is filtered and the filtrate at once mixed with an excess of calcium hydroxide and left for 12 hours to decompose any ethers. The filtrate is evaporated to dryness, the residue purified by redissolving in alcohol and the residue obtained from this is dissolved in water, when the nitric acid may be detected or estimated according to the usual methods.

A liver which had been moistened with a few grams of nitric acid

and left for three days was found to contain but one-fifth of the original quantity of nitric acid, the remainder having been converted most likely into xanthoprotein.

L. DE K.

Du Pont's Nitrometer. By GEORG LUNGE (*J. Soc. Chem. Ind.* 1901, 20, 100—101).—A reply to Pitman (this vol., ii, 192). It is stated that "Du Pont's five part nitrometer" is to all intents and purposes identical with the author's gasvolumeter (*Abstr.*, 1890, ii, 660).

L. DE K.

The Citric Acid Solubility of the Phosphoric Acid contained in Bone Meal. By THEODOR METHNER (*Zeit. angew. Chem.*, 1901, 134).—The citric acid solubility of the phosphoric acid contained in bone meal free from gelatin is equal to that contained in basic slag. In testing, it must be remembered that bone meal contains about twice the amount of phosphoric acid of the basic slag and consequently only 2.5 grams of the sample should be rotated for half an hour with 500 c.c. of a 2 per cent. solution of citric acid

L. DE K.

Estimation of Phosphoric Acid in Manures, Soils, and Ashes, by the Direct Weighing of the Phosphomolybdate. By NORBERT VON LORENZ (*Landw. Versuchs.-Stat.*, 1901, 55, 183—220).—The extracts are prepared as follows: (1) Phosphoric acid soluble in water: superphosphates (20) and double superphosphates (10 grams) per litre. (2) Citrate soluble phosphoric acid: Basic slag is extracted with ammonium citrate according to Wagner's method, and superphosphate by Petermann's method. (3) Phosphoric acid soluble in citric acid: Wagner's method with 2 per cent. acid. (4) Total phosphoric acid: Superphosphate and basic slag (5 grams) is treated with strong sulphuric acid (35 c.c.) or nitric acid (100 c.c.) and diluted to 500 c.c. All other phosphates containing more than 10 per cent. of phosphoric acid are extracted as just described. In the case of horn meal and manures containing less than 10 per cent. of phosphoric acid, the substance (10 grams) is treated with 50 c.c. of sulphuric or 100 c.c. of nitric acid, and diluted to 500 c.c. Soils (25 grams) are treated in the usual manner with not more than 200 c.c. of nitric acid; water (about 200 c.c.) is added, and, when cold, 10 c.c. of strong sulphuric acid. The whole is diluted to 500 c.c.

The following amounts of the different extracts are employed: (1) 10 c.c., (2) 15 and 10 c.c., (3) 15 c.c.; (4) superphosphates and basic slag, 15 c.c.; bone meal, &c., 20 c.c.; horn meal, &c., 15 c.c., and soils, 50 c.c.

The following solutions are prepared: (1) Pure dry ammonium molybdate (300 grams) is dissolved in a litre flask which, when cold, is filled to the mark; the solution is poured in a thin stream into a solution of 100 grams of pure dry ammonium sulphate in 1000 c.c. of nitric acid of sp. gr. 1.36 at 15°. The solution is left for 48 hours, filtered and kept in the dark. (2) A mixture of sulphuric acid of sp. gr. 1.84, 30 c.c., and nitric acid of sp. gr. 1.20 at 15°, 1 litre. (3) Ammonium nitrate (2 per cent.). Also nitric acid of sp. gr. 1.20 at 15°; alcohol (90—95

per cent.), free from dissolved matter and not alkaline ; and ether free from alcohol and sufficiently dry.

Estimation of Phosphoric Acid in the Extracts.—Extracts prepared with sulphuric acid (15—20 c.c.) are made up to 50 c.c. with nitric acid of sp. gr. 1.20 ; all other extracts (except soil extracts, of which 50 c.c. are employed) are made up to 50 c.c. with the mixture of nitric and sulphuric acids. The solution is then heated until the first bubbles are formed, and 50 c.c. of the sulphate-molybdate solution added. After about 5 minutes, the mixture is well stirred, left for 2—18 hours, or, when less than 3 mg. of phosphoric oxide is present, for 12—18 hours, and filtered through a platinum Gooch crucible (with a filter paper just covering the holes) under as much pressure as possible. After washing four times with ammonium nitrate solution, three times with alcohol, and three times with ether, the crucible is kept in a desiccator (without drying materials) under diminished pressure (100—200 mm.) for 30 minutes and weighed. The precipitate contains 3.295 per cent. of phosphoric oxide.

An apparatus is described in which several determinations can be carried on at the same time.

It is important for the ammonium molybdate to be as pure as possible. The amounts of extracts used for the separate determinations are such that they will never contain more than 50 mg. of phosphoric oxide ; larger amounts would render the drying with ether more difficult. The filter papers are rendered air dry by first heating at about 125° and then keeping them spread out for 24 hours. The ether-dried precipitate must be weighed as soon as it is taken out of the desiccator.

The method has the advantage over the direct citrate-precipitation method that the results are not affected by keeping citrate and citric acid extracts, containing silica, for several days. A further advantage is that the platinum crucibles are not injured in the process.

The results of determinations of phosphoric acid in solutions to which different compounds were added showed that no effect was produced by the various substances which may occur in manures and soils.

N. H. J. M.

Detection of Arsenic in the presence of Sulphites, &c. By JAMES F. SMITH (*Chem. News*, 1901, 83, 2—3).—Arsenic may be detected in the presence of compounds giving off hydrogen sulphide in the usual way in a Marsh apparatus, inasmuch as when the hydrogen sulphide and arsenide are heated together they react, hydrogen is set free and arsenic sulphide and sulphur are deposited in the tube or on the porcelain surface. The sulphur may be removed by carbon disulphide and the arsenious sulphide dissolved in ammonia, precipitated with hydrochloric acid, and tested. The original solution should be added 1 or 2 c.c. at a time to the acid and zinc, and an inch of the delivery tube in the centre should be kept red hot to avoid loss. Fifteen parts of arsenic per 1,000,000 have been detected in 5 c.c. of beer in presence of sodium hydrogen sulphite, and without previous treatment, by this means. This reaction also applies to antimony.

D. A. L.

Arsenic in Beer. By EDWARD W. T. JONES (*Chem. News*, 1901, 83, 25—26).—Two hundred and fifty c.c. of beer are evaporated to about 100 c.c., 25 c.c. of pure, strong hydrochloric acid are added, a piece of copper gauze 1 inch by $\frac{1}{4}$ inch is immersed, and the boiling continued; if the gauze is stained it is examined for arsenic in the usual way. For quantitative purposes, rolls of gauze 1 inch by $3\frac{1}{2}$ inches are used, and as one becomes blackened it is replaced by a bright one. The arsenic is removed by digesting the rolls of gauze in 5 c.c. of *N* sodium hydroxide to which 3 or 4 drops of 10 vol. hydrogen peroxide are added; the solution is tested, filtered, treated with 7 c.c. of *N* sulphuric acid, and saturated with sulphur dioxide which is then expelled by boiling. The warm solution is added to 50 c.c. of hydrogen sulphide solution and the gas passed for a time, the arsenious sulphide is washed, dissolved in hot dilute ammonia, filtered, evaporated to dryness, cooled, treated with three drops of water, just acidified with dilute hydrochloric acid, again dried, 3 c.c. of hydrogen sulphide solution added, again dried, rinsed successively with water, carbon disulphide, alcohol and water, again dried, cooled, and weighed; it is then treated with hot ammonia, any residue being weighed and deducted. D. A. L.

Arsenic in Beer. By JOHN RYDER and ALFRED GREENWOOD (*Chem. News*, 1901, 83, 61).—Two litres of beer are concentrated to 1 litre, and boiled with 3 or 4 grams of copper foil, and 166 c.c. of hydrochloric acid of sp. gr. 1.16; after an hour the beer is poured on to fresh copper for any further deposit. The coated copper is washed, dissolved in nitric acid, the excess of acid driven off, and the arsenic determined by the method recommended by Blair for the estimation of small quantities of the element in iron and steel. D. A. L.

Volumetric Estimation of Boric Acid. By H. LÜHRIG (*Chem. Centr.*, 1901, i, 538; from *Pharm. Central. Halle*, 1901, 42, 50—56).—The author confirms the opinion of Beythien and Hempel (*Abstr.*, 1900, ii, 313), and of Fischer (*ibid.*, 367), as to the accuracy of Jørgensen's process for the estimation of boric acid in foods (*Abstr.*, 1897, ii, 283). When testing meat, it is recommended to moisten the sample with strong aqueous sodium hydroxide, and to evaporate to dryness with addition of a little sodium carbonate with constant stirring; the dry mass is then burnt to ash. Gladding's process (*Abstr.*, 1898, ii, 483) offers no advantages over Jørgensen's method, being more complicated and less rapid. L. DE K.

Detection of Carbon Monoxide in the Air. By NATHAN ZUNTZ and S. KOSTIN (*Chem. Centr.*, 1901, i, 476; from *Arch. Anat. Phys.* (His-Eugelmann), *Physiol. Abt.*, 1900, *Suppl.*, 315—316).—A few litres of the air to be tested are collected in a glass bottle containing iron gauze moistened with ammoniacal water; after half an hour, the oxygen will be removed. If the residual gas is now passed through a solution of blood (1 : 100—200) carbon monoxide may be detected, even if the air only contained 1/40,000 part of that gas. L. DE K.

Detection of Minute Quantities of Carbon Monoxide in Blood and Air. By S. KOSTIN (*Pflüger's Archiv*, 1901, 83, 572—608).—A method of gas analysis is described with diagrams, by which minute amounts of carbon monoxide can be detected. Kunkel's tannin test is found to be the most delicate. Other methods, including Haldane's, are adversely criticised. Minute quantities of the gas are not absorbed by the blood if oxygen is present also. Cooling of blood to 0° increases its power of absorbing carbon monoxide. The method of detecting carbon monoxide in air is described in the preceding abstract.

W. D. H.

Estimation of Zinc. By W. HERZ (*Zeit. anorg. Chem.*, 1901, 26, 90—93).—See this vol., ii, 240.

Separation of Zinc from Nickel and Cobalt. By FREDERICK P. TREADWELL and G. H. KRAMERS (*Zeit. anorg. Chem.*, 1901, 26, 104—107).—The authors have examined Zimmermann's method (Abstr., 1880, 188; 1881, 12'), which consists in precipitating the zinc with hydrogen sulphide in the presence of ammonium thiocyanate. They find that accurate results are also obtained by precipitation in the presence of ammonium or potassium sulphate or chloride.

E. C. R.

Analysis of Samarskite. By ARTHUR GARFIELD LEVY (*Analyst*, 1901, 26, 64—67).—One gram of the finely powdered mineral is fused with 6 grams of potassium hydrogen sulphate in a platinum crucible until quite decomposed. When cold, the mass is treated with warm water until completely disintegrated, and the well-washed residue is strongly ignited and weighed as crude oxides of silicon, niobium, and tantalum.

The filtrate is mixed with some hydrochloric acid and then precipitated in a closed flask with an excess of ammonia; the filtrate, which generally retains some of the uranium and alumina, is boiled to recover it, and the filtrate from this examined, as usual, for calcium and magnesium.

The two ammonia precipitates are dissolved in hydrochloric acid, and the alumina is separated by means of sodium hydroxide; the rare earths are then thrown down as oxalates, and converted into oxides by ignition, and in the filtrate the iron and uranium are separated by means of ammonium sulphide and carbonate, the uranium being finally weighed as U_3O_8 , and also as UO_2 by way of control. An aliquot part of the crude oxides of silicon, niobium and tantalum, is again fused with potassium hydrogen sulphate; the resulting filtrate is treated as described above, and the residue freed from silica by treatment with hydrofluoric and sulphuric acids; the ignited oxides are dissolved in hydrofluoric acid, and the solution poured into a solution of potassium hydrogen fluoride, when a crystalline precipitate is formed which dissolves on heating (Marignac has stated that the oxides are insoluble in hydrofluoric acid, but the author finds them to be readily soluble in the warm acid). The solution is now evaporated to dryness on the water-bath; the residue is taken up with a little hot water, and allowed to crystallise. The crystals which contain potassium tantalum fluoride, and the liquid which contains the nioboxyfluoride, K_2NbOF_5 , are both evaporated with sulphuric acid, and the oxides of tantalum and niobium

so obtained are weighed. As neither oxide is quite pure, it must be freed from niobium or tantalum respectively by a second treatment with hydrofluoric acid.

Silica is estimated in another portion of the crude oxides, or in the ignited mineral itself, by the loss caused on evaporation with hydrofluoric and sulphuric acids. The separation of the rare earths into ceria and yttria groups is effected approximately as follows. The ignited oxalates are dissolved in hydrochloric acid with the aid of a little potassium iodide; a small residue may be left undissolved, and should be weighed and identified if possible. The solution is evaporated to dryness, the residue treated with a little water, and then with a saturated solution of potassium sulphate; after 2 days, the crystalline precipitate is washed with a solution of potassium sulphate, and the filtrate mixed, first with hydrochloric acid and then with ammonia in excess. The precipitate containing the oxides of the yttria group is washed, and then purified by dissolving it in hydrochloric acid and reprecipitating with ammonia, and finally ignited and weighed.

The precipitate containing the double potassium sulphates of the cerium group is dissolved in hydrochloric acid, and the oxides are then precipitated by ammonia, washed, ignited, and weighed.

The following result was obtained by the author in the analysis of a sample of samarskite: silica, 2·86; niobic oxide, 31·52; tantallic oxide, 16·63; ferric oxide, 10·68; aluminium oxide, 3·07; uranium trioxide, 12·13; calcium oxide, 3·34; magnesium oxide, 0·10; "cerium" oxides (free from true cerium oxide), 1·65; "yttrium" oxides, 14·32; "insoluble" oxides, 0·79; loss on ignition, 2·48. Total, 99·57 per cent.

L. DE K.

[Analysis of] Soils. By J. HAZARD (*Chem. Centr.*, 1901, i, 228—231; from *Landw. Jahrb.*, 29, 805—911).—The following method of soil-sampling is recommended. A hole 50 cm. wide and 35 cm. deep is made, the soil well mixed, and two samples (2·5 and 10 kilos.) weighed out. The smaller sample is kept, the larger sample being employed on the spot for determining stones (more than 10 mm.). The air dry sample is sifted through 10 and 3·5 mm. sieves. A portion (25—30 grams) is boiled for half an hour with fairly strong aqueous potash to remove the organic matter. Concretions of iron ore must be looked for in the residues on the sieves down to 0·15 mm.

The method employed for estimating kaolin depends on the fact that kaolin is not acted on by boiling hydrochloric acid, whilst it is decomposed by sulphuric acid. It is shown that soil treated with strong hydrochloric acid can only contain quartz, acid felspar, augite, and kaolin; the kaolin is conveniently extracted with sulphuric acid. The relation of alumina to ferric oxide or to lime will show the amount of augite if there is any present, and this is deducted from the total aluminium. Fineness of the sample is essential.

For ordinary agricultural purposes, the tenacity due to kaolin is determined by preparing four balls (30 grams each) which are then air-dried. One of the balls is placed with two marbles of equal size so as to form a triangle; the three are covered with a board and weights applied until the clay ball breaks. The other clay balls are

similarly treated and the mean of the four results adopted. The method gives very satisfactory results. N. H. J. M.

Chemical Investigation of Soil Samples from German East Africa. By ALBERT STUTZER (*Bied. Centr.*, 1901, 30, 1—3; from *Mitt. Landw. Inst. K. Univ. Breslau*, 1900; *Heft.* 3, 29. Compare Wohltmann, *Abstr.*, 1897, ii, 463, and 1898, ii, 251).—The following modifications have been made in the methods previously described. For the estimation of potassium, calcium, iron, aluminium, and phosphoric acid, 200 c.c. of the acid extract are evaporated down instead of 500 c.c. The addition of sodium chloride is omitted in determining potassium; an amount of extract corresponding with 60 grams of soil is used.

In determining calcium in presence of much iron and aluminium, 50 c.c. of the liquid are neutralised with ammonia and strongly acidified with oxalic acid at the ordinary temperature; the precipitate is washed with 2 per cent. oxalic acid. Iron and aluminium are estimated by precipitating with ammonia, dissolving in hydrochloric acid, and again precipitating with ammonia; the washed precipitate is ignited and weighed, and the amount of phosphoric acid deducted. Nitrogen is determined in 100 c.c. of the cold hydrochloric acid extract. The results of analyses of 25 samples are given.

N. H. J. M.

Estimation of Clay in Soil. By AIMÉ PAGNOUL (*Ann. Agron.*, 1901, 27, 94—96).—An amount of soil containing 5 grams of dry matter is washed three times with, altogether, 100 c.c. of dilute ammonia (1 c.c. of ammonia in 100 c.c. of water); the soil is rubbed with the finger against the sides of the dish and the whole allowed to settle for 10—15 seconds before the liquid is poured off. The soil is then boiled with the same solution for 2—3 minutes. When cold, more ammonia (1 c.c.) is added, and the liquid and soil transferred to a cylinder of 100 c.c. capacity (22 cm. from the bottom to the 100 c.c. mark) provided with a tap at the 20 c.c. mark. Distilled water is now added to make up to 100 c.c., after which the cylinder is violently shaken and allowed to rest for 5 minutes. The upper 80 c.c. are drawn off, treated with about 20 drops of acetic acid, and filtered. The precipitate is washed with water until free from lime, dried, and ignited. The weight of the residue multiplied by $100/80 \times 20$ gives the percentage of clay in the dry soil. A small amount of fine sand will be included, but the results are considered to be approximately correct. As a rule, the results vary from 10 to 20 per cent.; the highest amount of clay found was 57 per cent.

The filtrate from the clay precipitate may be utilised for determining the chalk present in an impalpable state.

N. H. J. M.

Estimation of Manganese in Ferro-Chromium Alloys. By J. T. (*Chem. News*, 1901, 83, 25).—One gram of the alloy is fused with a large excess of sodium peroxide, then treated with water, and the precipitate boiled repeatedly with water containing a small quantity of ammonium carbonate; it is then dissolved in nitric acid of sp. gr. 1.20 diluted with equal volume of water, and in presence of a large

quantity of solution of ferrous sulphate, the solution is oxidised with sodium bismuthate, and the filtered permanganate titrated with hydrogen peroxide as directed by Reddrop and Ramage (*Trans.*, 1895, **67**, 123—124. Compare Hillebrand and Stokes, *Abstr.*, 1900, **ii**, 763).—A. D. A. L.

Estimation of Ferrous Oxide in Silicates: Influence of Pyrites. By LUCIEN L. DE KONINCK (*Zeit. anorg. Chem.*, 1901, **26**, 123—124. Compare Hillebrand and Stokes, *Abstr.*, 1900, **ii**, 763).—A question of priority. E. C. R.

Vogel's Method for the Detection of Cobalt. By FREDERICK P. TREADWELL [and E. VOGT] (*Zeit. anorg. Chem.*, 1901, **26**, 108—110).—To test a nickel salt for cobalt, a solution of the salt is treated with a concentrated solution of ammonium thiocyanate and the mixture shaken with a few c.c. of amyl alcohol. In the presence of 0.02 mg. of cobalt, the amyl alcohol assumes a blue colour; if iron is present, the red colour of the ferric thiocyanate must be destroyed by shaking with sodium hydroxide.

The blue coloration is due to the salt $(\text{NH}_4)_2\text{Co}(\text{SCN})_4$, which crystallises from amyl alcohol in beautiful, blue needles. The potassium salt, $\text{K}_2\text{Co}(\text{SCN})_4$, is obtained in a similar manner (Rosenheim and Cohn, *Abstr.*, 1900, **i**, 381). E. C. R.

Reactions of Cobalt and Iron. By HUGO DITZ (*Chem. Zeit.*, 1901, **25**, 109—112).—See this vol., **ii**, 223.

Estimation of Chromium and Iron by Potassium-Iodide-Iodate Mixture. By ALFRED STOCK and CORNELIUS MASSACIU (*Ber.*, 1901, **34**, 467—469).—Chromium and iron may readily be estimated by the method previously described for aluminium (*Abstr.*, 1900, **ii**, 247). It is not necessary to have the iron in the ferric condition before precipitation. In the case of both metals, granular precipitates are obtained which can readily be filtered and washed. A further advantage is that even minute quantities of the metals are precipitated by this reagent, and do not tend to remain in solution as is the case when ammonia is employed. J. J. S.

[Detection of] Tungsten. By EDOUARD DEFACQZ (*Ann. Chim. Phys.*, 1901, [vii], 238—288).—See this vol., **ii**, 244.

Analysis of Tungsten- and Chrome-steel. Estimation of Tungstic Acid and its Separation from Silicic Acid. By OTTO HERTING (*Zeit. angew. Chem.*, 1901, 165—166).—McKenna's process for the estimation of tungsten and chromium in steels is criticised. The author gives a new process for the estimation of the tungsten. One to three grams of the ferrotungsten are treated with nitro-hydrochloric acid and evaporated twice with nitric acid on the water-bath. The mass is dried at 120°, and then dissolved in dilute nitric acid; the insoluble matter, consisting of tungsten trioxide, silica, and a little ferric oxide, is fused with sodium carbonate and the fused mass treated with water, when a residue of ferric oxide is left, which should be tested for traces of silica. The filtrate is evaporated twice with nitric acid, and the residue treated with dilute nitric acid, which leaves the silica and tungsten trioxide undissolved. These are collected and

weighed, and then fused with five times their weight of potassium hydrogen sulphate; the fused mass is digested with a cold solution of ammonium carbonate which dissolves the tungsten trioxide and leaves the silica undissolved; the latter is weighed and the former obtained by difference. The tungsten may also be estimated volumetrically by suspending a well-washed moist precipitate of silica and tungsten trioxide in hot water and titrating with normal sodium hydroxide, using phenolphthalein as indicator. One c.c. of the solution = 0.092 gram of tungsten. L. DE K.

Colorimetric Estimation of Titanic Acid. By JAMES BRAKES (*J. Soc. Chem. Ind.*, 1901, 20, 23. Compare Abstr., 1900, ii, 248).—This is a modification of Baskerville's method (Abstr., 1900, ii, 629), differing from it in so far that the residue left from the first filtrate is fused with potassium sodium carbonate and then heated with sulphuric acid. In preparing the standard solution, the chemically pure titanium dioxide is fused with the mixed carbonate instead of potassium hydrogen sulphate, and then heated with strong sulphuric acid. To standardise the solution, 10 c.c. are diluted with 25 c.c. of water and precipitated with ammonia, the precipitate is washed with hot water and ignited; the contents of the crucible are then moistened with a few drops of dilute sulphuric acid (1 : 1) and a few c.c. of hydrofluoric acid, and the whole is evaporated to dryness, ignited, and weighed. L. DE K.

Brandy Flavouring Essences. By ADOLF BEYTHIEN and PAUL BOHRISH (*Zeit. Nahr. Genussm.*, 1901, 4, 107—110).—A table is given showing the composition of some brandy flavourings. The alcohol was estimated by Hefelmann's process (Abstr., 1897, ii, 605). The residue from the light petroleum was tested for resinous matters, and piperine by Polenske's method. For the estimation of the fusel oil, 20 c.c. of the sample were mixed with 75 c.c. of absolute alcohol and then diluted with water to 100 c.c. Twenty-five c.c. of this mixture were diluted with 200 c.c. of water and 5 c.c. of aqueous potassium hydroxide and submitted to distillation; the distillate was then made up to 200 c.c., and after its sp. gr. had been taken it was tested with the usual precautions in Rose's apparatus. Two of the samples were found to contain piperine and one capsaicin. L. DE K.

The Furfuraldehyde Reaction in Brandy Testing. By TH. WETZKE (*Zeit. öffentl. Chem.*, 1901, 7, 11—16).—The author has examined a large number of brandies (cognac), pure and adulterated, and has come to the conclusion that the presence of furfuraldehyde gives no guarantee that the samples are really the product of the distillation of pure wines, particularly as furfuraldehyde is often added to spurious articles to deceive the analyst. The complete absence of furfuraldehyde in a sample is also not a safe proof of its adulteration. L. DE K.

Estimation of Glycerol. By JULIUS LEWKOWITSCH (*Analyst*, 1901, 26, 35—36).—The author has tried the process based on the isolation of the glycerol carbon by means of sulphuric acid, as proposed by Laborde (Abstr., 1899, ii, 816) and approved of by Jean (Abstr.,

1900, ii, 694). A large number of test experiments are given, showing that nothing like even approximate results can be obtained by this process. L. DE K.

Estimation of Sugar by Fehling's Solution, and Conversion of Cuprous into Cupric Oxide without the use of Asbestos Filters. By PAUL SOLTSIEN (*Chem. Centr.*, 1901, i, 343; from *Pharm. Zeit.*, 1901, 46, 28).—The mixture of Fehling's solution and sugar which has been heated as usual is diluted with about 3 volumes of boiling water. The cuprous oxide can then be collected on an ash-free paper filter. It is washed until the washings cease to redden phenolphthalein, then dried and ignited in a platinum basin. It is then dissolved in the smallest possible quantity of a mixture of sulphuric acid (5 parts) and nitric acid (3 parts), and the solution evaporated and ignited until the weight is constant. Copper sulphide may be converted into cupric oxide in a similar manner. M. J. S.

Kjeldahl's Method of Sugar Estimation. By RUDOLF WOI (*Chem. Centr.*, 1901, i, 343; from *Zeit. öffentl. Chem.*, 1900, 6, 514).—The author highly commends Kjeldahl's process (*Abstr.*, 1896, ii, 453, 580) as well as the extension of it by Jessen-Hansen (*Abstr.*, 1900, ii, 113), but considers that the absorption of carbon dioxide by the alkali hydroxide is a source of considerable error, and that the working out of complete tables for the employment of sodium carbonate instead of hydroxide, according to Müller's method, would be a great improvement. M. J. S.

Colour Reactions of Sugars. By CARL NEUBERG (*Zeit. physiol. Chem.*, 1901, 31, 564—573).—The behaviour of a number of synthetic sugars, namely, glycolaldehyde, glyceraldehyde, glycerose, *l*-erythrose, *i*-tetrose, *d*-lyxose, *d*-hydroxygluconic acid, aldehydomucic acid, and formose, towards α -naphthol, resorcinol, phloroglucinol, and orcinol in the presence of hydrochloric acid has been studied.

The α -naphthol test is given by all the sugars. The resorcinol test gives positive results with glycerose, *i*-tetrose, formose, and *d*-hydroxygluconic acid, and hence appears to work with ketoses only. The phloroglucinol test is given by all the sugars with the exception of glycolaldehyde, but the colour varies considerably in intensity. The orcinol test gives no characteristic colour with glycolaldehyde or *i*-tetrose, and appears to be the best test for pentoses. J. J. S.

Lindet's Process for the Estimation of Dextrose and Dextrin in Commercial Glucose. By JEAN MEUNIER (*Bull. Soc. Chim.*, 1901, [iii], 25, 250—251).—The author criticises Lindet's process (this vol., ii, 134) favourably, but finds that the somewhat tedious estimation of the total carbon by combustion may advantageously be replaced by a determination of the calorific power of the glucose. N. L.

Volumetric Estimation of Invert Sugar. By F. STOLLE (*Zeit. Ver. deut. Zuckerind.*, 1901, 111—117).—This method consists in precipitating a known volume of Fehling's solution with the invert sugar solution, and afterwards estimating the excess of Fehling's solution by titration with potassium cyanide in ammoniacal solution, the colour

being discharged owing to the formation of colourless potassium cuprous cyanide. To convert the copper of the residual Fehling's solution into ammoniocupric salt, sufficient of a mixture of 100 c.c. of concentrated ammonia solution with 50 grams of ammonium carbonate dissolved to 500 c.c. is added to give the liquid a deep blue colour. The potassium cyanide solution may be standardised by means either of pure copper sulphate or of pure copper dissolved in nitric acid. It is important that the same pipettes should always be employed for mixing the Fehling's solution or else that only accurately graduated pipettes be used. If necessary, the invert sugar solution is decolorised by means of basic lead acetate, the excess of lead being removed in the usual way. The method is carried out as follows. Ten or five grams of the sugar are dissolved in water and made up to 100 c.c., 50 c.c. of the solution being then mixed with 50 c.c. of Fehling's solution and the liquid boiled for exactly two minutes. The flame is removed and 50 c.c. of cold, air-free, distilled water added, after which the solution is transferred to a 250 c.c. flask, made up to volume at the normal temperature, and filtered. To 50 c.c. of the filtrate heated to 80—90° in a porcelain basin, 40 c.c. of the ammoniacal ammonium carbonate solution are added, and the standard potassium cyanide solution, containing conveniently about 25 grams per litre, run in until the solution is completely decolorised. The results obtained by this method agree well with those yielded by the ordinary gravimetric method in which the reduced copper is weighed, 9.5 grams of pure sucrose after inversion yielding 236.53 milligrams of copper by the volumetric method, and 236 by the gravimetric, whilst 20 grams of a raw sugar gave respectively, 53.9 and 54.9 milligrams by the volumetric and gravimetric methods. The new process can, of course, be applied to the estimation of all sugars which reduce Fehling's solution.

T. H. P.

Influence of Temperature on the Specific Rotation of Sucrose. By OTTO SCHÖNRÖCK (*Zeit. Ver. deut. Zuckerind.*, 1901, 106—111).—The author criticises Wiechmann's paper [*ibid.*, 1900, 902 (technical part)] on this subject.

Calculating from the temperature coefficient of the specific rotation of sucrose, previously found by the author to have the value 0.000217 (Abstr., 1900, i, 378), it is shown that if a normal sucrose solution, containing 26 grams in 100 c.c., be prepared at 20° and be read at t° in a saccharimeter whose quartz wedges are also at t° , then the reading must be increased by 0.065 ($t - 20$) in order to obtain the real hundred point at 20°; this only holds if t does not differ much from 20.

T. H. P.

Molasses and similar Products from Sugar Factories. By KARL ANDRLÍK, K. URBAN, and VL. STANĚK (*Zeit. Zuckerind. Böhm.*, 1901, 25, 247—272).—After giving a historical account of the work previously published on the analysis and composition of molasses, the authors describe the methods employed and the results obtained in the complete analysis of a number of samples of molasses before and after osmosis, osmose waters, and syrups. The paper does not admit of satisfactory abstraction.

T. H. P.

Chocolate-Flour. By ADOLF BEYTHIEN and HANS HEMPEL (*Zeit. Nahr. Genussm.*, 1901, 4, 23—25).—Analyses of six samples of artificially coloured prepared cocoas consisting chiefly of sugar and flour with but 9 to 16 per cent. of chocolate, and sold under fancy names.

The sugar was estimated by Woy's process (*Abstr.*, 1899, ii, 187). The total fatty matter was obtained by extraction, and the quantity of cocoa-fat and wheat flour-fat calculated from its iodine absorption figure, assuming that of pure cocoa-fat to be 34 and that of wheat flour-fat 115.

L. DE K.

Estimation of Pentosans by means of the Hydrochloric Acid Phloroglucinol Method. By E. KRÖBER (*Chem. Centr.*, 1901, i, 477—478; from *J. Landw.*, 1901, 48, 357—384).—This process gives correct results if the proper precautions are taken. The condensation product should be collected in a Gooch crucible and the wash water added in small portions and not until the precipitate looks almost dry; the washing must be continued until every trace of chlorine is removed. The precipitate should be dried for 4 hours at 98.5—100°, and the crucible afterwards cooled in a weighing tube under a desiccator.

L. DE K.

Detection of Oxycellulose. By MAX PHILIP (*Chem. Centr.*, 1901, i, 342; from *Zeit. öffentl. Chem.*, 1900, 6, 524).—Some cotton fabrics, which after bleaching in a bath of chloride of lime had been piled up and exposed to the air for some time, were found to have been partially converted into oxycellulose. When hot calendered, they showed yellowish to brownish stains, which gradually faded to a yellowish tone, and when heated with Fehling's solution cuprous oxide was deposited on the spots which had shown the brown stain. M. J. S.

Detection of Tragacanth and Dextrin in Cocoa and Chocolate and Approximate Estimation of Dextrin by Polarisation. By PAUL WELMANS (*Chem. Centr.*, 1901, i, 65; from *Zeit. öffentl. Chem.*, 1900, 6, 478—483).—Tragacanth is not likely to be used for adulterating cocoa or chocolate on account of its high price, but if its presence is suspected it may be detected by rubbing 5 grams of material, freed from fat, with dilute sulphuric acid, adding 10 drops of solution of iodine and a little glycerol, and examining under the microscope. If tragacanth is present, the field will be covered with a large number of blue tragacanth cells, which, however, closely resemble potato or wheat starch.

Adulteration with gelatin may be suspected when the sample contains an excess of water and more than 30—33 per cent. of proteids calculated on fat free matter. It may be readily detected by Onfroy's picric acid process (*Abstr.*, 1899, ii, 76).

Dextrin may be detected in the aqueous solution left when extracting the fat with ether according to the author's process, by adding 40 c.c. of alcohol to 10 c.c. of the filtrate. Its estimation is based on the fact that, although not precipitated by basic lead acetate, it is completely precipitated by an ammoniacal solution of the salt. By polarising the aqueous solution before and after addition of ammonia, the dextrin may be calculated by means of the expression

$d = (a - b)/2$, in which a represents the apparent total sugar and b the actual sugar present. It is necessary to divide by 2, as dextrin has twice the polarising power of sugar. The results are more accurate than those obtained by the usual gravimetric copper process.

L. DE K.

Use of Millon's Reagent. By OTTO NASSE (*Pflüger's Archiv*, 1901, 83, 361—368. Compare Plugge, *Arch. Pharm.*, 1890, 28, 9; Vaubel, this vol., i, 28).—The reagent is best prepared by mixing mercuric acetate solution with a few drops of a 1 per cent. solution of an alkali nitrite. It may be used either with or without the addition of acetic acid. Nitric acid should not be present. Hydrogen peroxide, alcohol, and large amounts of chlorides interfere with the colorations. Only a small amount of the reagent, and a moderate temperature are advisable.

Ortho-substituted phenols give a brownish-red colour, and the corresponding para-compounds a blue-red or even blue colour. Phenols which have both ortho- and para-substituents, for example, eugenol and vanillin, and even phenols with no para-substituents, such as thymol and xlenol, also give blue colours. Most specimens of phenol and salicylic acid give blue colours owing to the presence of small amounts of *p*-cresol and *p*-hydroxybenzoic acid.

Denigès' phenolaldehyde reaction (*Abstr.*, 1900, ii, 378) is readily given by tyrosine but not by peptone or by proteids. The reagent may be made by dissolving a little formaldehyde in concentrated sulphuric acid.

J. J. S.

Estimation of Cresol. By FRIEDRICH RUSSIG and GEORG FORTMANN (*Zeit. angew. Chem.*, 1901, 157—160).—Raschig's process for the estimation of *m*-cresol in mixtures (*Abstr.*, 1900, ii, 694) is recommended. The authors also use another method of French origin, which is briefly as follows. Fifty grams of the sample are treated with 125 grams of sulphuric acid of sp. gr. 1.84 contained in an Erlenmeyer flask; after 1 or 2 hours, the mixture is added drop by drop from a dropping funnel to 400 c.c. of nitric acid of sp. gr. 1.4 contained in a large retort and heated on a sand-bath to 60°, the flame being then removed. About 20 minutes after adding the last portions, the contents are poured into a large porcelain dish containing 200 c.c. of water, and the retort is rinsed with another 200 c.c. of water. After remaining overnight, the cake of trinitrocresol is pressed with a spatula, and then collected on a hardened filter, using the suction pump. After removing the adhering nitric acid by washing with 200 c.c. of water, the compound is dried at 95—100° and weighed. Fifty grams of pure *m*-cresol yield in this way 175.6 per cent. of the nitro-compound and 174 per cent. by Raschig's method. Like the latter, the process fails when the sample contains more than 10 per cent. of phenol.

Ditz's and Cedivoda's volumetric bromine process (*Abstr.*, 1900, ii, 54) has been submitted to a thorough investigation and found to be untrustworthy.

L. DE K.

Estimation of Cresol. By HUGO DITZ (*Zeit. angew. Chem.*, 1901, 160—165).—An elaborate reply to Russig and Fortmann (preceding

abstract), who, according to the author, have used too large an excess of bromine in their experiments. Other objections to their work are raised.

L. DE K.

Detection of Succinic Acid. By CARL NEUBERG (*Zeit. physiol. Chem.*, 1901, 31, 574—578).—The substance to be tested is evaporated down to a small volume with excess of ammonia, and then heated with zinc dust; if succinic acid was originally present, pyrrole is produced and may be tested for by the usual pine-wood splinter, moistened with hydrochloric acid. If succinates of heavy metals are present, it is advisable to add ammonium carbonate, or even ammonium phosphate, before the zinc dust. Other substances which are readily convertible into pyrrole must be removed before the test is applied. The more commonly occurring natural products which give the pyrrole test are albumin, hæmin, and indole derivatives, which may be readily removed.

J. J. S.

Estimation of Malic Acid. By ALBERT HILGER (*Zeit. Nahr. Genussm.*, 1901, 4, 49—50. Compare Abstr., 1900, ii, 768).—The following process is recommended for estimating malic acid in wines. One hundred c.c. of the sample are evaporated to one-third, and then rendered faintly alkaline by adding basic lead acetate. The precipitate which contains all the malic acid is collected, washed four or five times with cold water, and then dissolved in a little boiling dilute acetic or nitric acid. This solution is neutralised at the boiling point with excess of sodium carbonate, while a current of carbon dioxide is being transmitted. The filtrate is evaporated to 100 c.c., neutralised with hydrochloric acid, and then boiled for 10 minutes in an Erlenmeyer flask with 10 c.c. of a 5 per cent. solution of palladium chloride. After faintly acidifying with hydrochloric acid, the reduced palladium is collected in an Allihn tube, heated in a current of carbon dioxide, and weighed; 0.294 gram of palladium corresponds with 1 gram of malic acid.

L. DE K.

Estimation of the Nitrogen of Amino-acids in Urine. By MARTIN KRÜGER and JULIUS SCHMIDT (*Zeit. physiol. Chem.*, 1901, 31, 556—563).—The method is very similar to that described by Pfaundler (Abstr., 1900, ii, 674). Care must, however, be taken not to use too large an excess of phosphotungstic acid in precipitating the nitrogen compounds. The total nitrogen in 5 c.c. of the urine is determined by Kjeldahl's method. The total nitrogen in an equivalent quantity of the phosphotungstic acid filtrate is determined by the same method, and also the carbamide nitrogen in the same volume of filtrate is determined by heating with half its volume of concentrated sulphuric acid at 160—180° for 3—4 hours. The difference between the last two determinations gives the amount of nitrogen due to amino-acids.

J. J. S.

Action of Iodic Acid on Uric Acid. Estimation of Uric Acid. By H. BOUILLET (*Bull. Soc. Chim.*, 1901, [iii], 25, 251—255).—When uric acid is heated with excess of iodic acid in aqueous solution, it is completely decomposed into mesoxamide, carbamide, carbon dioxide, and ammonia, 1 mol. of iodine being also liberated for every 5 mols. of uric acid. If, however, the theoretical amount of iodic acid

is employed, the reaction is incomplete and alloxan is formed. Use is made of the first reaction for the estimation of uric acid in urine, but instead of distilling the precipitated barium urate with iodic acid solution and estimating the iodine in the distillate, as in Causse's process, the author prefers to remove the liberated iodine by boiling the liquid, and estimate the undecomposed iodic acid by adding potassium iodide and titrating with thiosulphate solution. The test analyses quoted are very satisfactory. N. L.

Detection of Cinnamic Acid in the Presence of Benzoic Acid. By ARMAND JORISSEN (*Ann. Chim. anal. appl.*, 1901, 6, 41—43).—After mentioning the permanganate test, the author describes a new reaction for the detection of cinnamic acid in officinal benzoic acid. One gram of the sample is dissolved in 10 c.c. of boiling distilled water; when cold, the liquid is filtered and the filter containing the benzoic acid is gently pressed. To the filtrate are now added 4 c.c. of a 5 per cent. aqueous solution of uranium acetate, and after closing the glass tube with a cork the liquid is exposed to light (preferably direct sunlight). Gradually, benzaldehyde is formed, easily recognisable by its odour. One per cent. of cinnamic acid may be thus detected; if large quantities are present, it is sufficient to mix a few decigrams of the sample with a few c.c. of the uranium solution, and to expose the mixture to light. L. DE K.

Detection and Estimation of Salicylic Acid in Wines. By ANTONIO J. FERREIRA DA SILVA (*Ann. Chim. anal. appl.*, 1901, 6, 11—12. Compare Abstr., 1900, ii, 695).—A reply to Pellet (this vol., ii, 207). The method proposed by Pellet and Grobert for the detection of salicylic acid in wines, although an excellent one for quantitative purposes, may sometimes show traces of this substance when it is really absent. L. DE K.

Composition of the Milk of Indian Cows and Buffaloes. By J. WALTHER LEATHER (*Analyst*, 1901, 26, 40—42).—Four tables are given showing the results of the analyses of milk of a large number of Indian cows from different localities and also of buffaloes' milk. The analysis includes the fat, proteids, lactose, and ash.

The milk from the Indian cows was found not to differ from rich English milk. The relation between the lactose, proteids, and ash agrees well with the proportions 13:9:2, and the non-fatty solids agree fairly well with those obtained by calculation, using Richmond's formula.

The samples of buffaloes' milk were characterised by an unusually high percentage of fat, 7 to 8 per cent. being common. The relation between the lactose, proteids, and ash is about 10:12:2 and the non-fatty solids agree also fairly well with those obtained by calculation.

L. DE K.

Refractive Power, Amount of Volatile Fatty Acids, and the Iodine Number of Butter Fat. By E. HOLM, A. V. KRARUP, and P. V. F. PETERSEN (*Bied. Centr.*, 1901, 30, 48—57; from 40^{de} Beretn. k. Vet. Landbohøjskoles Lab. landök. Forsög. Copenhagen, 1900, 1—46 and tables 1—56).—During four years (1895—1900), 7834

samples of butter, from 800 dairies, were examined. The refraction numbers of single samples varied from 48.6 to 54.9, but the average results for single dairies varied only between 50.2 and 52.9. As regards the influence of season, it is shown that from December to October there was a gradual increase from 50.2 to 52.8; in November there was a sudden fall to 51.0. In employing the refraction number as a criterion of purity, the time of year must, therefore, be taken into account.

In the case of samples of butter made at the same time, the amounts of fat and volatile fatty acids decrease as the refraction numbers increase. The variations are slight when the refraction numbers are between 48 and 51, but greater when the refraction numbers rise to 52—55.

The iodine numbers vary in accordance with the refraction number. The examination of butter from single cows showed that there may be considerable variations. The differences found at times in Danish butters may therefore be due to the nature of individual cows, and not to adulteration.

N. H. J. M.

Analysis of Butter Fat. By W. VON KLENZE (*Chem. Centr.*, 1901, i, 479; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 1901, 4, 77—80).—Higher figures are obtained when using the Leffmann-Beam method instead of the Reichert-Meissl process, the difference amounting to from 0.5 (or less) to 1.4 c.c. of *N*/10 alkali, and this is held to be caused by action of the alkaline glycerol on the non-volatile acids whereby volatile acids are generated. A copper distilling flask is preferred.

L. DE K.

Amount of Volatile Fatty Acids in Dutch Butters. By LODIEWYK TH. REICHER (*Zeit. angew. Chem.*, 1901, 125—127).—A large number of experiments are given extending over 7 years, showing that the Reichert-Meissl number of genuine Dutch butters may frequently fall below 25. Compare Kirchner and Racine (this vol., ii, 137).

L. DE K.

Halphen's Reaction for Cotton Seed Oil and the Behaviour of some American Lards towards the Same. By PAUL SOLTSEIN (*Zeit. öffentl. Chem.*, 1901, 7, 25—27).—The author now agrees that the use of amyl alcohol in the Halphen's test is advantageous, and heats the fat or oil to be tested for cotton seed oil with 20 per cent. of a 1 per cent. solution of sulphur in carbon disulphide, then adding half the volume of amyl alcohol. He has made a further improvement by not excluding the light during the heating in boiling water.

Several samples of genuine American lard which gave a decided Halphen test are supposed to be derived from pigs fed on cotton seed meal. Further experiments in that direction are promised.

L. DE K.

Examination of Varnish Resins. By JULIUS LEWKOWITSCH (*Analyst*, 1901, 26, 37—38).—The author has determined the acid and saponification numbers, unsaponifiable matter, iodine number (by

both iodine chloride, and bromine methods) and solubility in alcohol of several resins used in varnish making and has tabulated the results. As the resins are, however, not used in their natural state, but after having been submitted to a high temperature, the author has also determined the constants after heating the resins at 300°.

The following articles were tested : 6 samples of copal, 2 of sandarac, 2 of animi, 1 of kauri gum, 1 of mastic, 1 of dark shellac, 1 of dammar, 1 of amber, 1 of succinite (a species of amber) and 1 of ordinary rosin. The results show that these methods are of scarcely any practical use to analysts engaged in varnish testing.

L. DE K.

Detection of Antithermic Substances in Urine. By ARTHUR PETERMANN (*Ann. Chim. anal. appl.*, 1901, 6, 4—6).—Antithermic drugs are often administered to cattle to defeat the obligatory tuberculin test. Some of these, such as sodium salicylate, salol, and ethyl salicylate, decompose in the body and yield salicylic acid, which partially passes into the urine; antipyrine may also be detected in the urine.

Detection of salicylic acid.—The urine, if not already acid, should be feebly acidified with hydrochloric acid, and to 25 c.c. of the sample is then added one drop of a 10 per cent. solution of ferric chloride, when in the presence of salicylic acid the characteristic violet colour will make its appearance; it is discharged on adding more hydrochloric acid. *Detection of antipyrine.*—If the colour, instead of being violet, is blood-red, there is a likelihood of antipyrine being present; this is then tested for as usual by agitating the urine with chloroform or benzene.

Colouring matter in urine.—Occasionally, a clear garnet or a dark orange or intermediate colour is obtained which, however, resists the action of hydrochloric acid and finally yields a coloured precipitate.

L. DE K.

Estimation of Indican in Urine and its Clinical Significance. By WOLOWSKI (*Chem. Centr.*, 1901, i, 425; from *Deut. med. Woch.*, 1901, 27, 23).—The method resembles that used by the author for the evaluation of bleaching powder (*Abstr.*, 1900, ii, 165). Two hypochlorite solutions are used: the first contains 1 per cent. of active chlorine, the second 0.1 per cent., and they are contained in burettes which deliver 1 c.c. in exactly 20 drops. Ten c.c. of a 25 per cent. lead acetate solution are made up to 100 c.c. with the urine. The mixture is filtered, and 5 c.c. of the filtrate placed in each of five narrow test-tubes. These are treated with the hypochlorite solutions, beginning with 1 drop of the stronger, and rising by regular differences of 5 drops of the weaker. After 2 minutes, 5 c.c. of hydrochloric acid are added to each tube, and then 1 c.c. of chloroform. With normal indicanuria, the colour communicated to the chloroform should increase as far as the third tube, that in the fifth should be colourless. With hyperindicanuria, the colour will increase as far as the fifth tube. In that case, a fresh series is made with larger amounts of hypochlorite, until a point is reached at which the chloroform remains colourless. With hypoidicanuria, the chloroform will sometimes be colourless in the first tube. The tube giving the

strongest colour indicates the amount of indican present. The chlorine there employed is then multiplied by 0.025, and the total daily excretion of indican calculated. It is important to compare this with the total solids excreted; the latter may be calculated by the use of Haeser's factor; the excess of sp. gr. above unity $\times 2.33 =$ grams of solid matter per litre. In normal indicanuria, there should be present 0.1 mg. of indican for each gram of total solids. The clinical significance of the indican coefficient is discussed in the original paper.

M. J. S.

New Tannin Estimations. By LEOPOLD SPECHT and FRITZ LORENZ (*Chem. Zeit.*, 1901, 25, 5—6).—A mathematical and chemical investigation as to the merits of the safranine process for the estimation of tanning materials (*Abstr.*, 1900, ii, 515). It is shown that concordant results are obtainable when the directions are properly followed.

The best proportions for standardising the hyposulphite solution are: 0.45 gram of pure tannic acid, 0.54 gram of potassium-antimonyl tartrate, and 0.9 gram of safranine T in 1500 c.c. of water, to which are then added 35 c.c. solution of sodium hydrogen sulphite (of 1.96 sp. gr.), 1:10, and 33 c.c. solution of sodium hydrogen carbonate, 1:10. The mixture is then treated as previously directed. When testing the sample, it is advisable to take such a quantity as will represent as nearly as possible the same amount of tannin as used in the check experiment.

L. DE K.

Estimation of Tannic Acid, Organic and Mineral Acids in Tan Liquor. By FERDINAND JEAN (*Chem. Centr.*, 1900, ii, 1298; from *Ann. Chim. anal. appl.*, 5, 413).—The total acid is titrated with $N/20$ alkali, using lacmoid paper. A second portion is accurately neutralised with $N/10$ sodium carbonate, then mixed with 15 c.c. of a 2 per cent. solution of albumin, boiled, filtered, and the excess of alkali in the filtrate titrated at boiling temperature. The difference gives the tannic acid. In a third portion, tannic and gallic acids are precipitated by adding zinc oxide to exact neutrality, the precipitate is collected, washed with hot water, boiled with 20 c.c. of $N/10$ sodium carbonate, the zinc carbonate filtered off, and the excess of soda in the filtrate titrated. The difference from the second titration gives the gallic acid, that from the first the organic and mineral acids. A fourth portion is evaporated in platinum with 20 c.c. of $N/10$ sodium carbonate and incinerated. The ash is dissolved in water and titrated; the soda consumed indicates the mineral acid present, unless salts of organic acids are also present. In this case, a fifth portion is neutralised with baryta, boiled, filtered, and in the ash of the filtrate the alkali soluble in water is titrated with $N/10$ sulphuric acid.

M. J. S.

Analyses of Fruit Juices. By EDUARD SPAETH (*Zeit. Nahr.-Genussm.*, 1901, 4, 97—107).—A large number of analyses are given of pure and adulterated raspberry syrups. The chief object has been to detect whether for the preparation of the syrup a genuine raspberry juice or a diluted article has been used. The syrup is

generally made by bringing to the boil 35 parts of raspberry juice and 65 parts of cane sugar.

In a genuine article, the amount of ash obtained from 100 grams should not fall below 0.2 gram, and this should require for neutralisation not less than 2 c.c. of normal acid. The sugar free extract should not be less than 1.3 per cent. The acidity of the sample also affords a useful clue; 100 grams should require from 7.35 to 12.8 c.c. of *N* potassium hydroxide. L. DE K.

Analysis of Chicory Root. By JULES WOLFF (*Ann. Chim. anal. appl.*, 1901, 6, 8—10. Compare Abstr., 1900, ii, 37).—*Experiment with the juice.* 20—25 grams of the desiccated juice are dissolved in water, diluted to 100 c.c., acidified with a few drops of sulphuric acid, and fermented with yeast at 27°. The alcohol is then distilled off and estimated as usual. The residue in the distilling flask is made up to 100 c.c., a few more drops of sulphuric acid are added, and the contents heated for 15 minutes in the water-bath to complete the inversion of the inulin. When cooled, it is again fermented with yeast and the alcohol once more estimated. In this way, the author found the proportion between the alcohol derived from the readily fermentable matter and the same from the indirectly fermentable substance to be 1.70 : 1.

Experiment with the pulp.—(a) Sixteen grams of the dry pulp are heated in a 200 c.c. flask with 150 c.c. of water for 2 hours in the water-bath at 80°; when cooled to 27°—29°, it is fermented with yeast, and afterwards heated on the water-bath to expel the alcohol and the carbon dioxide. When cold, the liquid is made up to 200 c.c., filtered, and quantitatively tested for lævulose, both optically and with Fehling's solution. (b) Another portion of the sample is then treated in the same manner, but without previous fermentation. In this way, the author obtained for *b* the figure 66 and for *a* the figure 24.3, leaving 41.7 per cent. of inulins convertible into lævulose. L. DE K.

The Precipitation of Albumin in Urine by Clarifying Agents. By BRUNO GRÜTZNER (*Chem. Centr.*, 1901, i, 479; from *Pharm. Zeit.*, 1901, 46, 77—78).—The author states that the clarifying agents used in the analysis of urine, such as magnesium oxide, aluminium hydroxide, talc, lead peroxide, and even "kieselguhr," all precipitate notable quantities of albumin. The best way to get a clear sample is to allow it to settle, remove the supernatant liquid with a pipette, and then to filter through a double filter. Another good plan is to shake the sample with pulped and then redried blotting paper. L. DE K.

Action of Hydrogen Peroxide on Blood. Easy Means of Differentiating the Blood of Man from that of Animals. By S. COTTON (*Bull. Soc. Chim.*, 1901, [iii], 25, 255—257).—Quantitative study of the well known reaction between blood and hydrogen peroxide shows that it affords a ready means of distinguishing the blood of man and other animals. The following volumes of oxygen were evolved from 1 c.c. of defibrinated blood on treatment with 250 c.c. of 12 volume hydrogen peroxide: man, 580—610 c.c.; horse,

320—350 c.c. ; pig, 320—350 c.c. ; ox, 165—170 c.c. ; guinea pig, 115—125 c.c. ; sheep, 60—65 c.c. Slight differences are observed in favour of young and female animals, and blood which has been exposed to the air for a few hours yields more oxygen than either fresh blood or blood which has been exposed for a long time. The yield of oxygen is decreased in certain diseases, or by dilution with water. N. L.

Value of the Hæmatoporphyrin Test for the Forensic Detection of Blood. By CARL IPSEN (*Chem. Centr.*, 1900, ii, 1217 ; from *Vierteljahrschr. ger. Med. u. öffentl. Sanitätswesen*, 20, 1—11).—The author confirms the work of Kratter (*ibid.*, 1892, 4, 62), who stated that the spectroscopic hæmatoporphyrin test for blood answers very well for blood spots which have been subjected to a high temperature and are singed or charred, also for spots which are dried or have putrefied.

A microscopical examination of such blood spots will occasionally give a clue to the origin of the blood as shown by the presence of foreign particles. L. DE K.

Hæmin Crystals. By MAX RICHTER (*Chem. Centr.*, 1900, ii, 1215 ; from *Vierteljahrschr. ger. Med. u. öffentl. Sanitätswesen*, 20, 22—39).—The difficulty occasionally experienced in the detection of hæmin in blood is caused by the lessened solubility in acetic acid. The age of the blood spots, also the nature of the fabric, have in many cases a distinct bearing on the negative result of the hæmin test as the change of hæmoglobin into hæmin is accelerated or retarded.

The author advises waiting until the hæmochromogen has changed into hæmatin before proceeding to the hæmin test. L. DE K.

Detection of Bilirubin by Ehrlich's Diazo-reaction. By FR. PROSCHER (*Chem. Centr.*, 1901, i, 596 ; from *Centr.-Bl. inn. Med.*, 22, 169).—The diazo-reaction (Abstr., 1900, i, 571), which is a very sensitive test for bilirubin, is not produced by other bile pigments, such as bilifuscin, bilihumin, &c. On adding Ehrlich's reagent (Abstr., 1900, ii, 776) to a hydrochloric acid solution of bilirubin, the liquid becomes blue, and on making alkaline with dilute potassium hydroxide the colour changes to green ; in neutral solution, it is red. The author precipitates the bilirubin from 10 c.c. of urine by Méhu's method of saturating with ammonium sulphate, collects the precipitate on a filter, from which it is then dissolved by 96 per cent. alcohol, and uses the alcoholic solution strongly acidified with hydrochloric acid for the above reaction. The dilute potassium hydroxide should be poured carefully into the test tube, when at the point of contact a multi-coloured ring is formed in which the colours are in the order blue, red, and green.

The urine of icteric patients contains substances which interfere with the above reaction. M. J. S.

General and Physical Chemistry.

New Method of Characterising Colouring Matters: Application to Indophenols. By CHARLES CAMICHEL and PIERRE BAYRAC (*Compt. rend.*, 1901, 132, 882—885).—The authors have examined the absorption spectra of a large number of indophenols dissolved in alcohol, ether, carbon disulphide and chloroform respectively. When the wave-lengths are plotted as abscissæ and the coefficients of transmission as ordinates, a parabola is obtained with the convexity away from the axis of the abscissæ. The part of the curve corresponding with the red rays is much steeper than that corresponding with the green and blue rays, and the position of the minimum ordinate lies between $\lambda 610$ and $\lambda 535$, according to the nature of the indophenol and of the solvent. The lowest point of the curve, which corresponds with the minimum of transparency, and is the characteristic point, is accurately determined by means of a series of chords drawn parallel with the axis of the abscissæ. The position of the minimum of transparency is independent of the concentration of the solution for all compounds the coefficient of absorption of which is proportional to the concentration in accordance with Beer's law, but it varies with the nature of the solvent according to a law which is not, however, Kundt's law. The minimum is nearest to the red end of the spectrum when alcohol is the solvent, and nearest to the blue end when ether is the solvent. In chloroform, the minimum is nearer to the blue end than in alcohol, and in carbon disulphide it is nearer to the red end than in ether. Substitution of primary nitrogen for tertiary nitrogen displaces the minimum towards the blue end of the spectrum, whatever may be the solvent. A substitution in the ortho-position in the phenol from which the indophenol is derived causes a considerable displacement of the minimum of transparency, whilst a similar substitution in the meta-position causes little or no displacement (compare this vol., i, 296 ; ii, 100, 232). C. H. B.

Illumination of Different Kinds of Glass. By WALTÈRE SPRING (*Rec. Trav. Chim.*, 1900, 19, 339—349).—Ruby-glass is made by the addition of traces of gold chloride to an ordinary fused glass ; the glass so obtained is at first colourless and only assumes a ruby colour during subsequent prolonged heating. When an intensely luminous electric beam is passed tangentially through a small cylinder of the colourless gold-glass, practically no internal illumination is visible ; in the case of the ruby-glass, however, a yellowish-brown, luminous trace is produced, probably due to reflection from minute particles of metallic gold. The intensity of colour of the ruby-glass depends on the time of its reheating, and determines the intensity of illumination necessary to produce a visible trace ; the deeper the colour of the glass the less illumination is required. In the colourless glass, the gold probably exists in a state of extreme subdivision, and the reheating which produces the ruby colour brings about a coarser

colloidal aggregation, similar to that which takes place in gelatino-bromide plates during maturation (de Bruyn, *Rec. Trav. Chim.*, 1900, 19, 236).

Red glass coloured by copper, and yellow glass coloured by silver, show respectively dull brown and greyish luminous traces, due to the finely divided metals. Glasses coloured by silicates of iron, chromium, manganese, and cobalt show only a faint luminous trace, and, allowing for the presence of small air bubbles, are optically "void" (vide). Glasses which are colourless of themselves show a faint bluish trace and are yellow when viewed through a great length; they thus resemble media containing an extremely minute turbidity (compare Abstr., 1899, ii, 537, 585). Glass decolorised by manganese compounds shows an intensely green fluorescence, the luminous trace being green when the incident light is either violet or blue, but suppressed when it is green, yellow, or red. Glasses containing iron alone or manganese alone are not fluorescent.

W. A. D.

Apparatus for the Observation of Fluorescence and Opalescence. By M. TSVETT (*Zeit. physikal. Chem.*, 1901, 450—452).—A simple form of apparatus is described in which no lens is employed, the light being reflected upwards into a test-tube containing the liquid. With it eosin is seen to render water fluorescent even at concentrations of $1/10^9$.

L. M. J.

Induced Radioactivity and Gases made Active by Radium. By P. CURIE and A. DEBIERNE (*Compt. rend.*, 1901, 132, 768—770).—When a substance to be made radioactive, such as copper, is sealed up in a glass tube with the exciting radioactive substance, it gradually acquires a limited degree of radioactivity which is independent of the pressure and of the chemical nature of the gas in the tube. If, however, the pressure in the tube is extremely low and the vacuum is maintained during the experiment by the continued action of the pump, the substance does not become radioactive, and in the same conditions a substance which has previously been excited loses its activity. On the other hand, if the tube containing the radioactive substance and the other substance is made vacuous and then sealed up, excitation takes place after a time and reaches the same limit as under other conditions, whilst gas is evolved by the radioactive substance and produces a small pressure in the tube. If the radioactive substance is heated in a vacuum, the evolved gas can be collected. Although small in quantity, it is intensely radioactive, makes the glass of the containing tube luminous in the dark, acts instantly on photographic plates, and very rapidly discharges an electrified body. The glass of the tube that contains it soon becomes black (compare Abstr., 1900, ii, 125). The intensity of the radioactivity of this gas diminishes continuously, but very slowly; it is always very strongly active even ten days after it has been collected. It is noteworthy that the air of the laboratory in which these experiments have been carried on for some years has gradually acquired a higher and higher conductivity for electricity, a result which is probably due mainly to the continuous formation of radioactive gases analogous to those just described.

When hydrated barium chloride is heated in a vacuum, the water collected is radioactive, but when evaporated leaves no residue of a radioactive solid. If kept in a sealed tube, its radioactivity very slowly disappears. C. H. B.

Dielectric Constants of Nitriles. By HERMAN SCHLUNDT (*J. Physical Chem.*, 1901, 5, 157—169).—Solutions of salts in acetonitrile, propionitrile, and benzonitrile have a considerable electrical conductivity (see Dutoit and Friderich, *Abstr.*, 1899, ii, 350; Kahlenberg and Lincoln, *Abstr.*, 1899, ii, 397; Lincoln, *Abstr.*, 1900, ii, 6). In applying to these substances Nernst's rule of the connection between the dielectric constant of a solvent and its dissociating power (see *Abstr.*, 1894, ii, 266), the author has determined the dielectric constants of the following liquids at about 21° by Drude's method (*Abstr.*, 1897, ii, 438): hydrocyanic acid, 95; acetonitrile, 36·4; propionitrile, 26·5; butyronitrile, 20·3; isopropionitrile, 20·4; valeronitrile, 17·4; isovaleronitrile, 17·95; hexonitrile, 15·5; benzonitrile, 26·0; phenacetoneitrile, 14·9; *o*-toluonitrile, 18·4; pyridine, 12·4; quinoline, 8·8. The author concludes that Nernst's rule holds at best only for members of the same homologous series. The dielectric constant of a solvent is not the sole factor determining whether solutions in that solvent will conduct electricity or not. J. C. P.

The Nernst Formula for the E.M.F. of Concentration Elements. By HANS JAHN (*Zeit. physikal. Chem.*, 1901, 453—460).—The formula given by Arrhenius (this vol., ii, 144) for the *E.M.F.* of a concentration element is open to the objection that for concentrated solutions the transport numbers and isotonic coefficients are not known. For dilute solutions, however, it is shown that the formula becomes identical with that of Nernst, which Arrhenius held to be incorrect. The formula of Helmholtz also reduces to the Nernst expression for dilute solutions. The author again contests the supposition that the ratio μ/μ_∞ is a measure of the dissociation (*Abstr.*, 1900, ii, 522, 707). L. M. J.

Autoxidation and its Connection with the Theories of Ions and of the Galvanic Cell. By FRITZ HABER (*Zeit. Elektrochem.*, 1901, 7, 441—449).—The typical reaction in cases of wet autoxidation is, taking lead as an example, $\text{Pb} + \text{H}_2\text{SO}_4 + \text{O}_2 = \text{PbSO}_4 + \text{H}_2\text{O}_2$. This reaction may be caused to take place in a galvanic cell in which the anode consists of lead dipping into a saturated solution of lead sulphate in sulphuric acid. The change taking place at the anode is represented by the equation $\text{Pb} + 2F(+) = \text{Pb}^{++}$ ($F = 96540$ coulombs). The change occurring at the cathode would be $\text{O}_2 + 2\text{H}^+ - 2F(+) = \text{H}_2\text{O}_2$; such cathodes have been devised by Traube and by Richarz and Lannes. The total change in the cell would be represented by the equation $\text{Pb} + \text{O}_2 + 2\text{H}^+ = \text{Pb}^{++} + \text{H}_2\text{O}_2$, or, adding the SO_4^{--} ions to each side of the equation, $\text{Pb} + \text{O}_2 + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + \text{H}_2\text{O}_2$. The *P.D.* at the anode is about 0·284 volt in normal sulphuric acid; that at the cathode depends on the concentration of the hydrogen peroxide and may be taken to be about -0·8 volt. (The potential of the hydrogen electrode is taken

as zero in both cases.) The autoxidation cell would therefore have an *E.M.F.* of about 1 volt.

According to Traube, the typical wet autoxidation is represented by the equation $M + 2HO\cdot H + O_2 = M(OH)_2 + H_2O_2$. When the electrolytic dissociation of water is taken into account, this equation obviously represents a mechanism identical with that of the autoxidation cell. The theories of Engler and Wild and of Bach assume a different mechanism.

The fact that a solution of hydrogen peroxide is metastable, and decomposes completely into water and oxygen under the influence of catalytic agents, appears at first sight inconsistent with the fact that the *P.D.* of the hydrogen peroxide electrode is *lower* than that of the oxygen electrode. The potential is, however, determined by the reversible change which takes place at the electrode, in this case $2H\cdot + O_2 + 2F(-) \rightleftharpoons H_2O_2(a)$. An electrode at which the (as yet unrealised) reaction $2OH' + 2F(+) \rightleftharpoons H_2O_2(b)$, occurred would have a higher potential than the oxygen electrode, because the production of electrical energy by the combination of oxygen and hydrogen to form water may take place in one stage, represented by the equation $H_2 + O_2 = 2H_2O + 2(1.1 \times 2F)$, or in two stages represented by the equations (a) $H_2 + O_2 = H_2O_2 + 0.8 \times 2F$, and (b) $H_2O_2 + H_2 = 2H_2O + 2(1.3 + 2F)$.

The author considers that the different theories of wet and dry autoxidation may be reconciled with each other and with his results in the following statement. Oxygen always combines in undivided molecules. In dry processes, it unites with the oxidisable substance; in the typical wet processes, it combines with two hydrogen ions which part with their charges, two positive charges being simultaneously taken up by the oxidisable substance.

It is shown, also, that similar conclusions are reached by setting out from Nernst's formula for the potential of the oxygen electrode or from the hypothesis that the oxygen molecules first split up into oxygen atoms. This last assumption, however, agrees with the facts only when it is supposed that the formation of atoms from molecular oxygen is a slow process; this gives a plausible explanation of the fact that in dry autoxidations reactions of the type $M + O_2 = MO_2$ are more common than those of the type $M + O = MO$.

By the theory here developed, it is possible to predict the behaviour of most substances towards oxygen. Base metals and reducing agents, combined with an oxygen electrode, will give cells with a considerable *E.M.F.*, and such substances will undergo typical autoxidation; with more noble metals, the *E.M.F.* will be smaller; it becomes almost zero with mercury. With metals such as gold and platinum, and still more with substances giving high negative potentials, such as manganese dioxide, lead dioxide, &c., the reaction will be reversed, and instead of the change $M + O_2 + 2H\cdot = M\cdot\cdot + H_2O_2$, the reaction $M\cdot\cdot + H_2O_2 = M + O_2 + 2H\cdot$ will take place.

T. E.

Influence [of Benzyl Alcohol] on the Potential of Oxidation Cells. By KARL SCHAUM (*Zeit. Elektrochem.*, 1901, 7, 483—484).—The conversion of an alkali sulphite into a sulphate appears to take place

reversibly in accordance with the reaction $\text{SO}_4'' + 2\text{F}(-) \rightleftharpoons \text{SO}_3'' + \text{O}''$ (compare preceding abstract) at a platinum electrode immersed in a solution containing a mixture of sulphate and sulphite to which a drop of benzyl alcohol has been added. The reaction is not reversible in absence of the benzyl alcohol. The potentials of the electrodes are measured. T. E.

Electrochemical Relations between the Allotropic States of Metals, and especially of Silver. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 732–734).—When a plate of hammered silver foil and a plate of any of the other modifications of silver previously described (this vol., ii, 156) are immersed in a 10 per cent. solution of silver nitrate and connected externally with a conducting wire, an electric current is produced, the hammered silver foil being always positive with respect to the other modifications, which is in agreement with the thermochemical results (*loc. cit.*). After some time, the current ceases, either because both plates are brought to the same conditions, at the surface, by the deposition of silver from the solution, or because the other modification is brought superficially into the same condition as the hammered foil. C. H. B.

Electromotive Behaviour of Substances with several Stages of Oxidation. II. By ROBERT LUTHER (*Zeit. physikal. Chem.*, 1901, 385–404. Compare Abstr., 1900, ii, 705).—The various oxidation changes of chromium yield various *E.M.F.*'s and the following values are calculated: $\text{Cr}_{\text{metal}} \rightarrow \text{Cr}^{\cdot\cdot}$, +0.3 volt; $\text{Cr}_{\text{metal}} \rightarrow \text{Cr}^{\cdot\cdot\cdot}$, +0.2 volt; $\text{Cr}_{\text{metal}} \rightarrow \text{CrO}_4''$, -0.9 volt; $\text{Cr}^{\cdot\cdot\cdot} \rightarrow \text{CrO}_4''$, -1.8 volts; $\text{Cr}^{\cdot\cdot} \rightarrow \text{Cr}^{\cdot\cdot\cdot}$, +0.1 volt; $\text{Cr}^{\cdot\cdot} \rightarrow \text{CrO}_4''$, -1.4 volts. It is shown that if the intermediate oxidation compound exists under the experimental conditions, this compound is a stronger oxidising agent than the highest oxidation product and a stronger reducing agent than the lowest, and numerous examples are added. The equilibrium of cuprous and cupric salts in the presence of copper was investigated and the equilibrium constant deduced; $\text{Cu}^{\cdot\cdot}/\text{Cu}^2 = 1.5 \times 10^6$ at 25°, and from this the dissociation in saturated solution of cuprous salts is calculated, the values found being $\text{Cu}^{\cdot} \times \text{Cl}' = 2.2 \times 10^{-7}$, and $\text{Cu}^{\cdot} \times \text{Br}' = 8.2 \times 10^{-9}$. For the equilibrium concentrations, the *E.M.F.*'s for each change $\text{Cu} \rightarrow \text{Cu}^{\cdot}$, $\text{Cu} \rightarrow \text{Cu}^{\cdot\cdot}$, and $\text{Cu}^{\cdot\cdot} \rightarrow \text{Cu}^{\cdot\cdot\cdot}$ must be equal, and this was verified. The *E.M.F.* for $\text{Hg} - \text{HgCl}_2$ was calculated as 0.750 volt, and from this by independent methods the dissociation constant was deduced, the values obtained being 1.5×10^{-14} and 0.18×10^{-14} . L. M. J.

Electrochemical Studies of the Solubility of Precipitates containing Heavy Metals. By CL. IMMERWAHR (*Zeit. Elektrochem.*, 1901, 7, 477–483).—The *P.D.*'s between electrodes of mercury, copper, lead, cadmium, and zinc and saturated solutions of their less soluble salts were measured. The saturated solutions were obtained by precipitating the salts of the heavy metal with an excess of the reagent. From the potential difference, the concentration of the ions of the heavy metal in the solution may be calculated, and since the same excess of reagent was used in all cases, these concentrations are proportional to the solubility of the salts. Several salts gave values

varying between definite limits, corresponding doubtless with different conditions of the precipitate. The following table gives the order of solubility of the salts examined, the most soluble heading the list :

| Mercurous salts. | Cupric salts. | Cuprous salts. | Lead salts. | Cadmium salts. | Zinc salts. |
|------------------|---------------|----------------|--------------|-------------------------|-------------|
| Chromate. | Carbonate. | Chloride. | Chloride. | Chloride. | Iodide. |
| Phosphate. | Hydroxide. | Bromide. | Bromide. | Bromide. | Bromide. |
| Carbonate. | Oxide. | Iodide. | Thiocyanate. | Iodide. | Chloride. |
| Chloride. | Cyanide. | Thiocyanate. | Chromate. | Chromate. | Chromate. |
| Thiocyanate. | Sulphide. | | Iodide. | Phosphate. | Phosphate. |
| Bromide | | | Phosphate. | Hydroxide. ¹ | Hydroxide. |
| Oxide. | | | Carbonate. | Carbonate. | Carbonate. |
| Iodide. | | | Cyanide. | Cyanide. | Cyanide. |
| Cyanide. | | | Hydroxide? | Hydroxide. ² | Sulphide. |
| Sulphide. | | | Sulphide. | Sulphide. | |

(¹) Initial value.

(²) Final value.

T. E.

Laboratory Apparatus for Decomposition Voltages. By WILDER D. BANCROFT (*J. Physical Chem.*, 1901, 5, 133—136).—By means of a modified form of Le Blanc's method, the conditions under which metals can be separated, the existence of a complex ion, the conditions for a crystalline deposit, &c., can be easily investigated.

In the main circuit containing the electrolytic cell is interposed a mil-ammeter and the electrodes are connected with a high resistance voltmeter having a contact-key in this circuit. The voltmeter should be placed in series with another high resistance and under these circumstances the resistance of the solution can be neglected. The electrodes are platinum wires and the cell may be in the form of a beaker or a U-tube.

The measurements made are potential differences and not electromotive forces of polarisation. The value of the decomposition voltage can be arrived at by extrapolation to the point of zero current. The measurements are probably correct to about 1/50 volt.

The results obtained with solutions of zinc sulphate and sulphuric acid agree well with those found by Le Blanc. J. McC.

An Improved Melting Point Apparatus. By FREDERICK W. STREATFEILD and J. DAVIES (*Chem. News*, 1901, 83, 121).—To avoid inconvenience arising from acid fumes or from spirting or from the absorption of atmospheric moisture when taking melting points in sulphuric acid, the authors use a light dome-shaped glass cover of a size to rest lightly on the rim of an ordinary narrow beaker and furnished with two tubulated orifices for the passage of the thermometer and stirrer respectively. D. A. L.

Specific Heat of a Gaseous Mixture of Compounds in Chemical Equilibrium. By A. PONSOT (*Compt. rend.*, 1901, 132, 759—761).—A continuation of the author's previous paper (this vol., ii, 84), in which it is now deduced that the system the formation of which causes an increase of volume is that which tends to solely form the mixture when the temperature increases without limit either at constant volume or constant pressure. Its formation further

increases the specific heat of the mixture, this increase being greater at constant pressure than at constant volume. L. M. J.

Determination of the Specific Heats of Metals by their Rate of Cooling. MISS A. SERDOBINSKY and MISS A. EMELIANOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, ii, 23—28).—For the determination of the specific heat of a metal, the authors use a horizontal wire, the ends of which are fixed in rigid supports whilst the middle point is loaded to keep it taut. The wire is heated by the passage of a known current and then allowed to cool, the temperature at any instant being known from the length of the wire, which in its turn is calculated from the sag of the middle point. The authors' measurements yield for the mean specific heat of platinum the values 0.0319 and 0.0318. T. H. P.

Thermodynamical Observations. By HENRY J. S. SAND (*Zeit. physikal. Chem.*, 1901, 36, 499—507).—A discussion of the papers of Jahn (Abstr., 1900, 522, 707), Lehfelddt (this vol., ii, 4), and of Arrhenius (this vol., ii, 144) concerning the *E.M.F.* of concentration chains. L. M. J.

Thermochemistry of the Alloys of Copper and Zinc. By T. J. BAKER (*Proc. Roy. Soc.*, 1901, 68, 9—10. Compare *Proc.*, 1899, 15, 195).—By finding the difference between the heats of solution, in suitable solvents, of an alloy and of an equal weight of a mixture of the metals in the same proportions, the heat of formation of the alloy may be determined. The solvents used by the author were (1) chlorine water, (2) mixed ammonium and ferric chloride solutions, (3) mixed ammonium and cupric chloride solutions. Heat was developed in the formation of every alloy of zinc and copper tested. A maximum heat of formation (amounting to 52.5 cal. per gram of alloy) was found for the alloy with 32 per cent. of copper, corresponding with the formula CuZn_2 . The results, in general, confirm the existence of intermetallic compounds, and the values obtained are in accordance with those demanded by Lord Kelvin's calculation of the molecular dimensions of copper and zinc. [Compare Tayler, and Gladstone (Abstr., 1900, ii, 710).] J. C. P.

Dissociation and Thermochemistry of the Compound $\text{Al}_2\text{Cl}_6 \cdot 18\text{NH}_3$. By E. BAUD (*Compt. rend.*, 1901, 132, 690—692. Compare this vol., ii, 161).—The compound $\text{Al}_2\text{Cl}_6 \cdot 18\text{NH}_3$ is a very unstable substance obtained by treating the salt $\text{Al}_2\text{Cl}_6 \cdot 12\text{NH}_3$ with ammonia at -23° ; it cannot exist at the ordinary temperature, for its dissociation pressure is 760 mm. even at -14.6° , whilst at 0° the value of this constant is 1790 mm. Determinations of the dissociation pressure have also been made at other temperatures, and the results agree with the values calculated by means of Clapeyron's formula.

The specific heat of the compound is 0.4494, and its heat of solution in water is 15.88 Cal. The heat generated by the addition of 6NH_3 to $\text{Al}_2\text{Cl}_6 \cdot 12\text{NH}_3$ is 49.62 Cal., or 8.27 Cal. per mol. of ammonia; the latter value is employed in the calculation of the dissociation pressures by Clapeyron's formula. The variation of entropy deduced either from

this expression or from the curve of dissociation pressures is 32.004, a value corresponding with those obtained from other ammonio-chlorides.

G. T. M.

Heat of Fermentation. By ADRIAN J. BROWN (*J. Fed. Inst. Brewing*, 1901, 7, 93—103).—The heat of fermentation of maltose was determined to be 121.9 cal., a result in fairly close accordance with those obtained by Bouffard with dextrose (*Abstr.*, 1896, ii, 12). As calorimeter, a large copper fermenting vessel with a capacity of 216 cubic feet was used, this was coated with a layer of wood 1 inch thick, the influence of the external temperature being thus reduced to a minimum.

R. H. P.

Depression of the Freezing Point in Solutions containing Hydrochloric and Sulphuric Acids. By JAMES BARNES (*Trans. Roy. Soc. Canada*, 1900, [ii], 6, Sec. III, 37—54. Compare *Abstr.*, 1900, ii, 522).—If Δ be the depression of the freezing point in a mixture containing equal volumes of solutions of the two acids, and if H_2SO_4 be regarded as dissociating into 3 ions, then $2\Delta = M_1n_1(1 + \alpha_1) + M_2n_2(1 + 2\alpha_2)$, where M_1 and M_2 are molecular depressions, n_1 and n_2 the concentrations of the simple constituent solutions, α_1 and α_2 the ionisation coefficients in the mixture. For the latter, the conductivity of the simple constituent solutions has been determined at 0° , and α_1 and α_2 then calculated by a modification of MacGregor's method (*MacGregor, Trans. Roy. Soc. Canada*, 1896, [ii], 2, 69; Barnes, *Trans. Nova Scot. Inst. Sci.*, 1899, 10, 124). The values of Δ , calculated from the above equation, agree well, up to an average concentration of 0.2 gram-molecule per litre, with the values based on actual determination of the freezing point depression for the mixtures. The method used in the freezing point determinations was essentially that of Loomis (*Ann. Phys. Chem.*, [ii], 51, 500; *Abstr.*, 1900, ii, 335), and the author's results for dilute solutions of both acids agree with those of Loomis better than with those of Jones.

J. C. P.

Determination of the Decrease of Vapour Tension of a Solution of Sodium Chloride at Higher Temperatures. By A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 503—507. Compare *Abstr.*, 1900, ii, 389, 708).—The author, by means of a Bremer oil tensimeter, has measured the decrease of vapour tension of sodium chloride solutions between 50° and 80° . The actual lowering of the vapour pressure is compared in each case with the theoretical lowering, and van't Hoff's factor i is thus determined. It is found that i increases with the concentration of the solutions.

J. C. P.

Determination of the Decrease in Vapour Tension, and of the Lowering of the Freezing Point of Solutions which are not very dilute. By A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 507—514).—With the help of van Laar's formulæ (*Zeit. physikal. Chem.*, 1894, 15, 457) for the decrease of vapour tension and the lowering of the freezing point in solutions, the author compares Raoult's freezing point observations (see *Abstr.*, 1899, ii, 203) with his own vapour tension results. The agreement is good in the case of sucrose, bad in the case of sodium chloride solutions. When the

values of i for sodium chloride solutions are compared, it is seen that Raoult's results show a fall in the value of i with increasing concentration, whilst the author's results point to the reverse being the case (see preceding abstract). The author considers Raoult's observations faulty, and points out that Chrustchhoff (see this vol., ii, 86) observed an increase of the molecular depression of the freezing point with increasing concentration in the case of potassium bromide solutions. It is also pointed out that there are freezing point determinations in which a minimum value of i has been found (compare Jones and Chambers, *Abstr.*, 1900, ii, 262; Chambers and Frazer, *Abstr.*, 1900, ii, 526).

J. C. P.

Vapour Tension of Ternary Mixtures. II. By FRANZ A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1901, 36, 413—449).—A continuation of the extended and fuller treatment of the author's previous paper on the same subject (this vol., ii, 146; see also *ibid.*, 224).

L. M. J.

Relation between the Temperature Changes of the Specific Volumes of Liquid and Saturated Vapour. By JOHANNES D. VAN DER WAALS (*Zeit. physikal. Chem.*, 1901, 36, 461—468).—The expression for this relationship is $dv_1/\beta_1 = -dv_2/\beta_2$ where β_1 , β_2 are the compressibility coefficients at constant temperature. Although the accuracy cannot be rigorously proved experimentally, yet sufficient data are obtained from the determinations of Young and Amagat to prove at least the approximate correctness of the equation.

L. M. J.

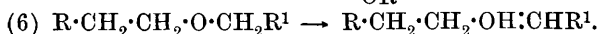
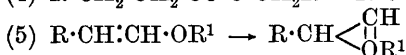
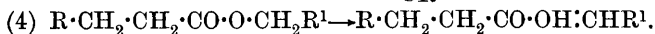
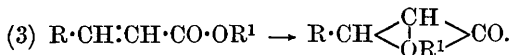
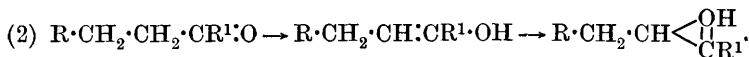
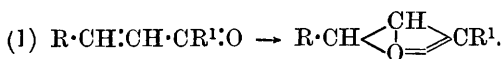
True Density of Chemical Compounds and its Relation to Composition and Constitution. II. Oxygenated Compounds. By INNOCENTIUS I. KANONNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 61—82 and 95—127. Compare *Abstr.*, 1900, ii, 134).—The author has determined or calculated the "molecular density" (*loc. cit.*) of a large number (about 450) of oxygenated organic compounds, and from the results obtained conclusions are drawn as to their constitution. The compounds are divided into the three classes: (1) alcohols, (2) carbonyl compounds containing the group CO, and (3) ethers, comprising substances with the molecular grouping C—O—C. For each of these classes a formula has been arrived at for the molecular density, the general expression for the three classes being: $(MD) = nC + mH + pO - 27.3n - 21.7(p+1) - 3.87 - (2p^{11} - 1)3.87 + 4.84p^1 \pm x$, where n , m , and p are the numbers of atoms of carbon, hydrogen, and oxygen respectively present in the molecule; C, H and O represent the corresponding molecular densities, and have the values $C=67.0$, $H=0.967$, and $O=126.44$; p^1 and p^{11} are the numbers of atoms of oxygen present in the carbonyl and ether forms, and x a coefficient representing the influence of ring-formation and of multiple linking between carbon atoms; -27.3 is the change produced in the molecular density of carbon, and -21.7 in that of oxygen, when these elements enter into combination with others; -3.87 represents the influence of the formation of a chain of atoms.

The determination of the molecular density affords a good means of

deciding whether an oxy-compound has an enolic structure. Thus in the case of mesityl oxide, the molecular density has the value 316.49, the number calculated for the constitution $\text{CMe}_2\text{:CHAc}$ being 326.07; the enolic formula, $\text{CMe}_2\text{:CH}\cdot\text{C(OH):CH}_2$, however, leads to the value 316.43. The action of certain solvents in bringing about enolisation is also clearly shown by a study of the molecular density. Thus, for example, the value for acetone is 209.53, whilst 97.27 and 76.3 per cent. aqueous acetone solutions give respectively the numbers 208.72 and 198.91, the calculated value for the enolic formula for acetone, $\text{OH}\cdot\text{CMe}\text{:CH}_2$, being 198.37. Similar relations hold for other compounds containing a carbonyl group in the molecule.

In a large number of cases, however, the differences existing between the experimental and calculated numbers are too considerable to be explainable on the assumption that the compounds have an enolic structure. In such compounds, which all contain the group $\text{C}\cdot\text{O}\cdot\text{C}$, the experimental numbers are always less than the calculated, and it is found that the differences are approximately multiples of 7.74. These deviations are assumed to be due to the existence of quadrivalent oxygen atoms in the molecules of the compounds concerned. Acetone, for instance, in more dilute solutions than those mentioned above, has a less value for its molecular density than that corresponding with the enolic form. This is assumed to be due to its being converted, to a greater or less extent, into the allo-modification having the structure $\text{CMe}\text{<}\begin{smallmatrix} \text{CH}_2 \\ \text{OH} \end{smallmatrix}$, the calculated value for which is 184.72.

Similarly, allyl phenylpropiolate has a molecular density of 698.48, whilst the value calculated from the ordinary formula is 743.58; for the constitution $\text{C}_5\text{H}_{11}\cdot\text{O}\text{<}\begin{smallmatrix} \text{CPh} \\ \text{CO} \end{smallmatrix}\text{>C}$, however, the value would be 702.95. A number of other similar examples are given. The process of enolisation is thus assumed by the author to be the first phase in a structural change of the molecule, the principal types of compound undergoing such a change being the following:



With some compounds, it is necessary to assume the existence in the molecules of a sexavalent oxygen atom.

A number of alcohols, ethers, aldehydes, ketones, acids, and esters show differences between the experimental and calculated values of their molecular densities which are regarded as due to polymerisation

of their molecules, the numbers calculated from the polymeric formulæ being in good agreement with those actually obtained. Acetic acid, for example, has a molecular density 276.68, whilst the number corresponding with the constitution $\text{O} \begin{smallmatrix} \text{CMe}(\text{OH}) \cdot \text{O} \\ \text{CMe}(\text{OH}) \cdot \text{O} \end{smallmatrix} \text{CMe}(\text{OH})$ is 277.74. Many other similar instances are given.

In a table at the end of the paper are collected for 442 oxygenated compounds the observed molecular densities, together with the values calculated according to the author's views and the percentage differences between the two sets of numbers. The agreement is in most cases very good, and in no case does the difference exceed 1 per cent.

T. H. P.

Dissociation Studies. II. By WILDER D. BANCROFT (*J. Physical Chem.*, 1901, 5, 182—192).—A paper mainly theoretical. The chief points are, (1) The displacement of equilibrium zones by catalytic agents; (2) the general discussion of systems in which three modifications occur; (3) the application of Duhem's theory to the case of acetaldehyde, based largely on the experimental work of Kekulé and Zincke (*Annalen*, 1872, 162, 125); (4) the different relative accelerating effects of different catalytic agents as shown experimentally.

J. C. P.

Dialysis in certain Liquids in which Indiarubber, but not Parchment, swells up. By AUGUSTIN WRÓBLEWSKI (*Chem. Zeit.*, 1901, 25, 222—223).—Ethereal solutions can be dialysed through a membrane of certain kinds of (pure) indiarubber; for example, from an ethereal solution of yolk of egg a yellow colouring matter diffuses out whilst lecithin remains. A rubber membrane can also be used with light petroleum; not so with benzene, in which it dissolves. In methyl, ethyl, propyl, butyl, and amyl alcohols, the rubber swells up but little and the dialysis is very slow. In chloroform and carbon disulphide, pure rubber swells up very much and readily tears.

C. F. B.

Equilibrium between Ester, Water, Acid, and Alcohol. By HANS EULER (*Zeit. physikal. Chem.*, 1901, 36, 405—412).—The constant of hydrolysis of a salt, that is, the value $C_{\text{acid}} C_{\text{base}} / C_{\text{salt}} C_{\text{water}}$ is equal to $K_4 K / K_2 K_3$ where K , K_2 , K_3 , K_4 are respectively the dissociation constants of water, acid, base, and salt. Similarly, the constant of hydrolysis of an ester should be inversely proportional to the dissociation constants of the acid and the alcohol. Determinations were made of the constants of hydrolysis for the methyl, ethyl, and propyl esters of formic, acetic, propionic, chloroacetic, and hydrochloric acids. It was found that the methyl esters were least, the ethyl esters most hydrolysed, and that the hydrolysis was greater the greater the dissociation constant of the acid. This result is not in accord with the theoretical conclusions, and the explanation given is based on the supposition that the dissociation of ester, acid, and alcohol may take place according to either of two schemes, thus, $\text{CH}_3\text{CO} \cdot \text{O}' - \text{C}_2\text{H}_5$ and $\text{CH}_3\text{CO} - \text{OC}_2\text{H}_5$; $\text{CH}_3\text{CO} - \text{OH}'$ and $\text{CH}_3\text{CO} \cdot \text{O}' - \text{H}$; $\text{C}_2\text{H}_5 \cdot \text{O}' - \text{H}$ and $\text{C}_2\text{H}_5 - \text{OH}'$.

L. M. J.

Decomposition by Sodium of Organic Halogen Compounds dissolved in Ethyl Alcohol. By RICHARD LOWENHERZ (*Zeit. physikal. Chem.*, 1901, **36**, 469—498).—The previous work (Abstr., 1900, ii, 338) has been extended to ethyl alcohol solutions and also to lithium and potassium, whilst some additional halogen compounds have also been employed, namely, *p*-bromoaniline, *p*-bromobenzoic acid, chloroform, and *p*-dibromobenzene. The results are in general similar to those previously obtained; the constant *k* is, however, smaller for lithium than for sodium, whilst for potassium it is of about the same magnitude. Satisfactory constancy is not obtained, however, for potassium, probably owing to secondary reactions. It was found that the extent of the surface of the sodium did not influence the reaction; addition of water causes a marked diminution, 2 per cent. reducing the constant by about 40 per cent. The author draws attention to the importance of such determinations in the case of many organic preparations.
L. M. J.

Tendency of the Atomic Weights to Approximate to Whole Numbers. By R. J. STRUTT (*Phil. Mag.*, [vi], 1, 311—314).—The author shows by a calculation of probabilities that the atomic weights tend to approximate to whole numbers far more closely than can reasonably be accounted for by any accidental coincidence, and believes that the complete rejection of Prout's hypothesis is unwarranted.
J. C. P.

Determination of Atomic Weights, based on the laws of the Transparence of Matter for X-Rays: Atomic Weight of Indium. By LOUIS BENOIST (*Compt. rend.*, 1901, **132**, 772—774).—The method previously described (this vol., ii, 215, 216) has been applied to indium and to indium acetylacetonate, and the transparence of indium for X-rays, whether it is in the metallic state or in the form of a compound, shows conclusively that its atomic weight is 113.4, and not 75.6. This result is confirmed by the behaviour of the indium and its compound to the "soft" and "hard" X-rays respectively; it falls into the same group as silver and cadmium.
C. H. B.

Inorganic Chemistry.

Boiling Point of Liquid Hydrogen, determined by Hydrogen and Helium Gas Thermometers. By JAMES DEWAR (*Proc. Roy. Soc.*, 1901, 68, 44—54).—A constant volume thermometer, charged with hydrogen or helium, has been used. It is shown by a number of experiments that either a simple or a compound gas at an initial pressure somewhat less than one atmosphere may be relied on to determine temperatures down to its own boiling point in the constant volume gas thermometer. The mean values of separate determinations give -182.5° as the boiling point of oxygen, and

-252.5° as that of hydrogen. The latter is lower than the value -238.4° previously obtained with a platinum-resistance thermometer (*Proc. Roy. Soc.*, 1898, **64**, 227). J. C. P.

Preparation of Chlorine from Sodium Chlorate. Preparation of Phosphorus Trichloride. By CARL GRAEBE (*Ber.*, 1901, **34**, 645—652).—The method of Gooch and Kreider (*Abstr.*, 1894, ii, 445) was modified by employing a higher temperature (compare Schacherl, this Journal, 1877, i, 47) and replacing the potassium chlorate by the more soluble sodium chlorate. A round-bottomed flask is employed, to the neck of which are sealed a delivery tube, and another tube which is bent down and dips under water, so as to serve as a safety tube; a dropping funnel passes through a cork in the neck of the flask, and has its tube drawn out at the end to a capillary tube and bent upwards. If only a comparatively small quantity of chlorine is required, as for an analytical operation, 50—55 c.c. of hydrochloric acid of sp. gr. 1.10 are placed in a flask of 70—75 c.c. capacity, whilst in the funnel, the recurved tip of which dips under the surface of the acid, a solution of sodium chlorate in water (1 : 2) is placed. The acid is heated to a temperature just below that of ebullition, and maintained at that temperature, whilst the chlorate solution is allowed to flow in at a suitable rate. For larger quantities, larger flasks are employed, and acid of sp. gr. 1.12. The heating may be continued for a little while after all the chlorate has been added; the acid can be utilised until the amount of hydrogen chloride has fallen to 5 per cent., when 16 and 20 grams of chlorine will be obtained from 100 c.c. of acid of sp. gr. 1.10 and 1.12 respectively. The gas contains about 5 per cent. of chlorine peroxide; if necessary, it may be freed from this by passing it through a glass tube heated to a dull red heat (when the gas delivered contains oxygen), or by washing it with water, 50 c.c. of which suffice for 3 grams of the gas.

In the preparation of phosphorus trichloride, it is convenient to pour some trichloride over the phosphorus before passing the chlorine in. The gas should enter the flask containing the phosphorus through a T-tube; the gas enters through the side limb, whilst a glass rod slides in the wide vertical limb, adapted to it by a cork, and serves to push down any pentachloride temporarily formed, which otherwise might block the tube. Red phosphorus may be used; there is then greater liability to blocking of the tube, but the trichloride obtained is quite free from phosphorus. With 51 grams of yellow phosphorus, 85 of phosphorus trichloride, and chlorine from 1000 c.c. of hydrochloric acid of sp. gr. 1.12 and 200 grams of sodium chlorate, the addition of the chlorate lasted an hour, and the heating was continued for 10 minutes longer; the gain in weight was equal to the theoretical, and on distilling the product 220 grams of additional trichloride were obtained. For drying the chlorine, only one wash-bottle with strong sulphuric acid was used. C. F. B.

Transformation of Hypochlorites into Chlorates. By FRITZ FOERSTER (*J. pr. Chem.*, 1901, [ii], **63**, 141—166. Compare *Abstr.*, 1899, ii, 278).—In the previous paper (*loc. cit.*), it was suggested

that the conversion of hypochlorite to chlorate is effected by free hypochlorous acid, which oxidises the hypochlorite ions: (1) $\text{ClO}^- + 2\text{HOCl} = 2\text{H}^+ + 2\text{Cl}^- + \text{ClO}_3^-$. As a method is now available of estimating hypochlorous acid in the presence of hypochlorites by means of hydrogen peroxide, which only reacts with the acid, the reaction expressed by the above equation has been studied quantitatively and its velocity determined.

The known action of chlorine in effecting the transformation of hypochlorite is shown to depend on the production of free hypochlorous acid. Thus when chlorine is led into a dilute neutral solution of hypochlorite the "hypochlorite oxygen" is largely increased. (2) $\text{Cl}_2 + \text{H}_2\text{O} + \text{NaOCl} = \text{NaCl} + 2\text{HOCl}$. The double value required by the equation is never reached, as the hypochlorous acid developed converts some of the hypochlorite into chlorate, a process which plays a more prominent part the more concentrated is the original solution of hypochlorite.

Consideration of equation (1) shows that the concentration of the hypochlorous acid remains constant owing to the union of the hydrogen ions, which are produced, with hypochlorite ions already present in the solution. (3) $2\text{H}^+ + 2\text{ClO}^- = 2\text{HClO}$. The concentration of the hypochlorite ions then alone changes. Therefore from equation (1) the formation of chlorate must be a unimolecular reaction, and the velocity constant for a given concentration of hypochlorous acid must be given by the equation of the first order, $k = 1/t \cdot \log(a/a-x)$. Finally, this constant must be proportional to the square of the concentration of the acid, when this concentration is varied. The experiments of which the results are given in the paper fully confirm this view. The concentration of the hypochlorous acid remains constant until the whole of the hypochlorite has disappeared. The values obtained for k are constant for dilute solutions of hypochlorites. For higher concentrations, the hypochlorite is not initially completely dissociated; as the transformation proceeds, the proportion of the hypochlorite dissociated increases, with the result that k no longer remains constant throughout the experiment. It is further shown that the rate of the transformation increases rapidly with increase of the concentration of hypochlorous acid, and with rise of temperature. Thus for three similar solutions respectively at the temperatures 19.5° , 35° , and 49° , k has the value 0.001326, 0.00552, and 0.0205. Light accelerates the formation of chlorate, but not to a marked extent.

The influence of chlorides on the rate of transformation of hypochlorites is studied. Low chloride concentration has little influence, but higher concentrations (above $2N$) produce a marked increase in the rate. Chlorides appear to exercise a specific influence, as other normal salts, although increasing the rate of transformation (probably by causing change in the solvent), have not such marked effect.

The action of hypochlorous acid on alkali chlorides, producing chlorate and free chlorine, is discussed, and the experiments of von Tiesenholt are considered (this vol., ii, 154). The reaction is best

expressed by the equation $\text{NaCl} + 6\text{HOCl} = \text{NaClO}_3 + 3\text{H}_2\text{O} + 3\text{Cl}_2$; and it is shown that other normal salts are without action.

K. J. P. O.

Action of Ozone upon Substances containing Sulphur and upon Sulphur. By THEODOR WEYL (*Chem. Zeit.*, 1901, 25, 292).—Ozonised air was led into solutions or suspensions of various substances in water or acetic acid. With potassium thiocyanate, the solution remains clear, but sulphuric acid is formed; with diphenylthiocarbamide, sulphur is deposited; with thiocarbamide, sulphur is deposited, and sulphuric acid formed; with sulphur, sulphuric acid is formed; with thiophen, phenylthiocarbamide, and egg-albumin, no effect is noticeable.

C. F. B.

Improvement of Küster's Hydrogen Sulphide Apparatus. By GUSTAV FRERICHs (*Arch. Pharm.*, 1901, 239, 118—121).—In Küster's apparatus (*Abstr.*, 1893, ii, 134) the acid drops on to a thick layer of iron sulphide, and is completely used up as it trickles down over it. It has the disadvantage that a good deal of acid enters at first before the steady evolution of gas begins. This is obviated by interposing a small vessel between the large reservoir of acid and the bottle of sulphide; this vessel has a valve that will admit air but permit none to escape; it can also be connected temporarily with the air by means of a rubber tube and pinchcock. It is first filled with acid from the reservoir whilst its connection with the sulphide bottle is closed; the latter connection is then closed whilst that with the sulphide bottle is opened, the delivery tube of the latter being opened at the same time. To render any but a slow stream of gas impossible and so prevent waste, the end of the delivery tube is packed with cotton-wool. The sulphide bottle is provided with a safety tube dipping under mercury.

C. F. B.

Hydrate of Sulphuryl Chloride. By ADOLF BAEYER and VICTOR VILLIGER (*Ber.*, 1901, 34, 736—738).—A crystalline hydrate, $\text{SO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$, is produced on adding sulphuryl chloride to ice-cold water; the substance resembles camphor in appearance and melts at the ordinary temperature. It is only slightly soluble in cold water, and is but slowly decomposed by this solvent at 0° ; on allowing the temperature of the mixture to rise, the crystals disappear and the original chloride is regenerated, the inverse change taking place when the reagents are cooled. The hydrate is stable even in the presence of sodium hydrogen carbonate, and the formation of the crystals is observed on adding sulphuryl chloride to an ice-cold aqueous solution of this alkali. The stability of the hydrate towards water and the hydrogen carbonate seems to indicate that the elements of water are not added to the acid chloride in such a manner as to form the dihydroxide, $\text{SOCl}_2(\text{OH})_2$, for such a substance has a constitution corresponding with chlorosulphonic acid, $\text{SOCl}(\text{OH})$, a compound instantly decomposed in aqueous solutions.

G. T. M.

Interaction of Potassium Permanganate and Alkali Thiosulphates in Neutral Solutions. By LEONARD DOBBIN (*J. Soc. Chem. Ind.*, 1901, 20, 212—218).—Earlier work on this subject is discussed

at some length, and new experiments are described from which the following conclusions are drawn. In cold, neutral solutions, the action gives rise to a dark brown, flocculent precipitate and a neutral solution, not an alkaline one, as stated by Spring and Levy (*Bull. Acad. Roy. Belg.*, 1876, [ii], 42, 103). The quantity of potassium permanganate necessary to produce a permanent pink coloration with a known weight of thiosulphate varies slightly with the conditions of temperature and the rate of addition of the solution, and is always less than the amount theoretically necessary to form the sulphate, assuming the permanganate to be reduced only to manganese dioxide. The precipitate formed is a manganite and always contains some manganese in a lower state of oxidation than the dioxide; when thoroughly washed, it contains the alkali metal and manganese in varying proportion depending on the conditions of its formation, along with traces of sulphur compounds, and is able to slowly decolorise dilute solutions of potassium permanganate. The solution filtered from the manganite contains sulphate and tetrathionate in the mol. ratio of about 6:1, this ratio being nearly the same at every stage of the interaction; this fact proves that the sulphate is not formed from the tetrathionate by further oxidation, as assumed by Fordos and Gelis (*Ann. Chim. Phys.*, 1848, [iii], 22, 60) and by Spring and Levy (*loc. cit.*), but that two oxidations occur simultaneously. The solution containing the tetrathionate, when free from thiosulphate, slowly decolorises dilute potassium permanganate, but complete oxidation of the tetrathionate to sulphate does not occur even after prolonged boiling with an excess of the oxidising agent.

In neutral solution, there is no evidence of any other sulphur compound being formed than sulphate and tetrathionate (compare Lückow, *Abstr.*, 1893, ii, 164).

W. A. D.

Temperature of Ignition of Phosphorus. By F. H. EYDMANN jun. (*Rec. Trav. Chim.*, 1900, 19, 401—407).—This was measured by gradually raising the temperature, by means of a water-jacket, of melted phosphorus submerged in water, whilst a current of air or oxygen was bubbled through the fused mass; time readings of the temperature of the water above the phosphorus were taken, the ignition point being that at which a rapid increase of temperature was observed. This was found to be at 45.0—45.2° in air, oxygen, or air diluted with an equal volume of carbon dioxide, the temperature of ignition thus being independent of the concentration of the oxygen.

W. A. D.

Composition of Amorphous Phosphorus. By FRIEDRICH FITTICA (*Chem. Zeit.*, 1901, 25, 261. Compare this vol., ii, 236).—If dry, amorphous phosphorus is heated with lead oxide and amorphous boron, a reaction takes place between 140° and 205°; water is evolved and lead sulphate and boron nitride are formed. If boron trioxide is used instead of lead oxide, arsenic also is formed, with or without antimony. The author thinks that amorphous phosphorus is a compound of nitrogen, sulphur, and hydrogen, and that it may have the formula N_2SH_2 ; he remarks, however, that his experiments do not furnish a complete proof of this quantitative composition.

C. F. B.

Detection of Nitrogen in Arsenic. Transformation of Arsenic into Antimony. By FRIEDRICH FITTICA (*Chem. Zeit.*, 1901, 25, 259. Compare Abstr., 1900, ii, 476, 651).—A reply to Arnold and Murach (this vol., ii, 236). C. F. B.

Preparation of Arsenic free from Antimony. By N. A. ORLOFF (*Chem. Zeit.*, 1901, 25, 290).—Pure arsenic is obtained free from antimony by precipitating pure crystalline sodium arsenate with magnesia mixture, dissolving the precipitate in hydrochloric acid, and precipitating it fractionally with ammonia; the middle fraction is washed, dried, and sublimed with sugar-charcoal.

The yellowish-red deposit, obtained by Fittica (this vol., ii, 236) in the reaction of arsenic with amorphous boron, was presumably Bettendorf's variety of arsenic, which is formed at a low temperature and is transformed into the ordinary grey variety when heated.

C. F. B.

Action of Hydrogen on Realgar and the Inverse Reaction Influence of Pressure and Temperature. By H. PÉLABON (*Compt. rend.*, 1901, 132, 774—777. Compare Abstr., 1900, ii, 652).—When a mixture of realgar and arsenic is heated with hydrogen (*loc. cit.*), the pressure of the gas has no influence on the limiting composition of the gaseous mixture, but if arsenic is absent, the value of R is affected by the pressure. The lower the pressure the higher the value of R , and the more does it differ from the value obtained in presence of excess of arsenic. If the realgar is not completely volatilised, its mass is without influence on the value of R . In the action of hydrogen sulphide on arsenic, on the other hand, the value of R is lower the lower the pressure of the gas. These results agree qualitatively with the thermodynamic theory of dissociation.

C. H. B.

Action of Sodium Ethoxide and Alkalis on Arsenic Pentasulphide. By RUDOLPH F. WEINLAND and P. LEHMANN (*Zeit. anorg. Chem.*, 1901, 26, 322—344).—When arsenic pentasulphide is dissolved in cold solutions of alkali hydroxides, ammonia, or barium hydroxide, thioarsenate and thiooxyarsenates are formed. The reaction which takes place is expressed by the equation $4\text{As}_2\text{S}_5 + 24\text{KOH} = 3\text{AsS}_2\text{O}_2\text{K}_3 + 2\text{AsSO}_3\text{K}_3 + 3\text{AsS}_4\text{K}_3 + 12\text{H}_2\text{O}$. Dithiooxyarsenates are formed in greater quantity than monothiooxyarsenates, which is not in accordance with McCay's results (this vol., ii, 95). By the action of sodium hydroxide on a mixture of arsenic trisulphide and sulphur, the same salts are obtained, and this is the best method of preparing dithiooxyarsenates.

Sodium hydroxide and arsenic trisulphide yield arsenic, thioarsenate, and mono- and di-thiooxyarsenates. When alcoholic sodium hydroxide is employed, mono- and di-thiooxyarsenates and arsenates are formed.

A solution of arsenic pentasulphide in an alkali hydroxide, when treated with acid, does not give a quantitative precipitate of arsenic pentasulphide; the thiooxyarsenates are only partially decomposed in the cold and on warming are converted into arsenious acid, which remains in the solution.

Thioarsenates are completely decomposed by a solution of potassium antimonyl tartrate in potassium sodium tartrate, and a quantitative precipitate of antimony tetrasulphide, Sb_2S_4 , is obtained. By this reagent it is therefore easy to estimate thioarsenates in the presence of thiooxyarsenates, since the latter salts are not affected.

E. C. R.

Preborates. By SIMEON M. TANATAR (*Zeit. anorg. Chem.*, 1901, 26, 343—346).—By the electrolysis of orthoborates, a solution is obtained at the anode which decolorises permanganate and liberates iodine from potassium iodide, whence the author concludes that a small quantity of perborate is formed, this being contrary to the observations of Constam and Bennett (this vol., ii, 17). It is, however, at present impossible to distinguish between the reactions for hydrogen peroxide and perborates, but since hydrogen peroxide converts borates into perborates, the formation of hydrogen peroxide must necessarily be accompanied by the formation of perborates.

E. C. R.

Perborates. By EMIL J. CONSTAM and J. CORA BENNETT (*Zeit. anorg. Chem.*, 1901, 26, 451).—In answer to Tanatar's criticisms (preceding abstract), the authors claim to be the first to show that perboric acid is monobasic. With regard to the formation of perborates by the electrolysis of borates, they point out that such a dilute solution of hydrogen peroxide as is formed under these conditions is not capable of converting borates into perborates.

E. C. R.

Reducing Action of Carbon on Metallic Compounds. By OCTAVE BOUDOUARD (*Bull. Soc. Chim.*, 1901, [iii], 25, 282—287. Compare Abstr., 1899, ii, 287, 365, 417, 595).—Intimate mixtures of dry, purified carbon with various metallic compounds were heated in porcelain at known temperatures, ranging from 445° to 1150° , and the gases evolved collected and analysed. The substances experimented with were calcium carbonate, barium carbonate, barium sulphate, zinc oxide, nickel oxide, and cupric oxide. The results obtained are in accord with Berthelot's observations on the reduction of alkali sulphates by hydrogen and carbon, and with the author's previous study of the reaction $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$ (Abstr., 1899, ii, 417, 596). The reducing action is not due directly to carbon, probably because of its polymerised state, but to carbon monoxide, a trace of which is always present to start the reaction. The carbon dioxide formed is then decomposed by carbon with the regeneration of carbon monoxide, and so on indefinitely.

N. L.

Cæsium Compounds. By CAMILLE CHABRIÉ (*Compt. rend.*, 1901, 132, 678—681).—*Cæsium bromide* is obtained in a pure state by mixing together solutions of cæsium sulphate and barium chloride so that the latter salt is in slight excess, evaporating the filtered liquid to dryness, calcining the residue and repeatedly crystallising the product; the smaller and less defined isotropic crystals which first separate correspond with the formula CsBr . *Cæsium iodide* is obtained in a like manner, the solutions containing the salt being evaporated at 60° under reduced pressure; it separates in well-defined, white, cubical

crystals. *Cæsium hydrogen fluoride*, CsHF_2 , prepared by dissolving pure cæsium carbonate in hydrofluoric acid and allowing the solution to evaporate, first over sulphuric acid and then over quicklime, separates in long, hygroscopic needles and has a distinctly acid reaction. *Cæsium fluoride*, CsF , obtained by calcining the preceding salt in the presence of ammonium fluoride at a temperature short of redness, crystallises in the cubic system. *Cæsium chromate*, Cs_2CrO_4 , crystallises in light yellow needles from the solution obtained by mixing together silver chromate and cæsium chloride dissolved in boiling water; the *dichromate*, $\text{Cs}_2\text{Cr}_2\text{O}_7$, produced by adding the equivalent amount of chromium trioxide to a solution of the preceding salt, separates in bright red, sparingly soluble crystals. G. T. M.

Action of Hydrogen Peroxide on Silver Oxide. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1901, 34, 749—755).—The authors' experiments confirm Thénard's statement that a mixture of hydrogen peroxide and silver oxide always evolves more oxygen than would be liberated by the action of a catalyst on the peroxide. Practically equal amounts of oxygen are obtained from a given quantity of hydrogen peroxide whether it is treated with metallic silver or spongy platinum; the yield is always somewhat short of the theoretical because the solution retains a portion of the gas in a state of supersaturation.

Hydrogen peroxide evolves more oxygen when treated with silver oxide than with spongy platinum, the excess being produced by the reduction of the silver oxide; the greater portion of the gas is eliminated by shaking the mixture, and subsequent treatment of the solution and precipitate with dilute sulphuric acid fails to set free any more of the gas. This result contradicts Berthelot's hypothesis as to the intermediate formation of the peroxide Ag_4O_3 (compare Abstr., 1880, 441, and this vol., ii, 8).

When hydrogen peroxide is added to silver oxide, the action takes place initially in accordance with the equation $\text{H}_2\text{O}_2 + \text{Ag}_2\text{O} = 2\text{Ag} + \text{O}_2 + \text{H}_2\text{O}$; subsequently a portion of the peroxide is decomposed catalytically by the finely divided silver produced. There is no experimental justification for assuming the existence of the silver peroxide. G. T. M.

Solubility of Lime in Water at Different Temperatures. By A. GUTHRIE (*J. Soc. Chem. Ind.*, 1901, 20, 223—224).—Solubilities are given in grams of lime per 100 c.c. of saturated lime water for every 5° of temperature from 5—100°, and the relationship of these values with those of other observers dealt with. W. A. D.

Reducing Properties of Magnesium and Aluminium. By ANDRÉ DUBOIN (*Compt. rend.*, 1901, 132, 826—828).—Magnesium filings, when moistened with water and primed with a little of the dry metal, take fire and burn with great brilliancy; the flame obtained with a mixture of coarsely powdered aluminium and water, when fired by a priming of magnesium powder, is even more brilliant. A mixture of alumina (1 mol.) and aluminium (4 atoms) when ignited at one point

becomes incandescent throughout, with the formation of the suboxide Al_2O . These reactions take place with equal readiness in an atmosphere of hydrogen, when the mixtures are fired by means of an oxygen flame burning in this gas. The oxides of the alkaline earth metals are, under these conditions, reduced by magnesium or aluminium, the reaction taking place most readily in the case of baryta. A mixture of boric oxide and magnesium, when ignited in hydrogen, yields boron mixed with a certain amount of magnesium boride; a similar reaction occurs when the magnesium is replaced by aluminium; in this case, a priming of magnesium and barium oxide is required. A mixture having the composition $\text{Ca}_3(\text{PO}_4)_2 \cdot 8\text{Mg}$ burns with incandescence, either in air or hydrogen; in the latter gas, a solid yellow hydrogen phosphide is deposited on the sides of the experimental tube; the product of reduction evolves spontaneously inflammable phosphine on treatment with water. The calcium phosphate is not completely reduced when the magnesium is replaced by an equivalent amount of aluminium. A mixture of potassium dichromate (1 mol.) and aluminium ($3\frac{2}{3}$ atoms), when ignited, continues to burn vigorously, with evolution of potassium vapour; this metal, when set free in an atmosphere of hydrogen, absorbs the gas so rapidly that a partial vacuum is produced in the apparatus. G. T. M.

Copper Antimonates. By A. E. DELACROIX (*Bull. Soc. Chim.*, 1901, [iii], 25, 289—290).—The antimonates of copper, and the double antimonate of copper and ammonium, have already been described (*Abstr.*, 1900, ii, 145). A potassium copper antimonate and a basic copper antimonate have now been obtained. N. L.

Preparation of Aluminium Chloride, Bromide, and Iodide. By GABRIEL GUSTAVSON (*J. pr. Chem.*, 1901, [ii], 63, 110—112).—Aluminium chloride and bromide are obtained by gently warming aluminium foil, contained in a hard glass tube, in a current of chlorine or bromine; the product in each case distils over into a receiver. The iodide is very readily prepared by leaving a mixture of equivalent proportions of aluminium foil and iodine, with three times its weight of carbon disulphide, in a stoppered vessel for about 2 days, at the ordinary temperature. The iodide dissolves in the carbon disulphide as soon as it is formed. W. A. B.

Compounds of Aluminium Bromide with Bromine and Carbon Disulphide. By WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 91—94. Compare *Abstr.*, 1900, i, 323).—By the action of bromine on aluminium bromide in carbon disulphide solution, a compound, $\text{AlBr}_3 \cdot \text{Br}_4 \cdot \text{CS}_2$, is obtained as an extremely hygroscopic, amorphous, yellow powder with a faint greenish tint; it is quickly turned red by sunlight or by a small quantity of moisture. When heated in a sealed capillary tube, it melts at $86-90^\circ$ with evolution of reddish-brown vapours which condense on the upper parts of the tube; if the heating be continued to above 100° , the carbon disulphide and bromine are given off, aluminium bromide being left. The compound is soluble in ether, carbon disulphide, ethyl bromide, ethylene dibrom-

ide, or benzene. By the action of water, it gives rise to Hell and Urech's trithiobromide, $C_2Br_6S_3$ (Abstr., 1882, 706, 945).

T. H. P.

Chemical Action between Dry Hauerite and Various Metals at the Ordinary Temperature. By GIOVANNI STRÜVER (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 124—127).—When hauerite is left for some time in contact with silver, the latter becomes coated with a black layer of silver sulphide. Preliminary experiments show that a similar action takes place when metals other than silver are used. The investigations are being continued.

T. H. P.

Constituents of Commercial Ferrosilicons. By PAUL LEBEAU (*Compt. rend.*, 1901, 132, 681—683).—The iron silicide produced by heating iron with excess of copper silicide corresponds with the monosilicide, $FeSi$, and the commercial specimens examined did not contain more than 33 per cent. of silicon (compare De Chalmot, Abstr., 1899, ii, 488). The monosilicide is sometimes found in leaf-like masses of crystals situated in the geodes found in the commercial silicides, these substances also containing the compounds Fe_2Si and $FeSi_2$.

The *disilicide*, $FeSi_2$, produced by treating iron and excess of silicon in the electric furnace, is isolated in the form of small, lustrous crystals.

The commercial silicides contain small quantities of carbon, chiefly in the form of graphite, although traces of amorphous carbon are sometimes noticed. There is no evidence, however, that carbon replaces silicon in atomic proportions in these products in the manner indicated by Jouve (compare next abstract). The presence of amorphous carbon is almost invariably associated with that of manganese and the other impurities of the silicides; calcium, sulphur, and phosphorus may also have some influence on the condition of the carbon contained in the silicides.

G. T. M.

Iron Silicides. By ADOLPHE JOUVE (*Bull. Soc. Chim.*, 1901, [iii], 25, 290—293).—Commercial iron silicon alloys contain their silicon in the form of the two silicides, Fe_2Si and $FeSi$, characteristic crystals of which are frequently observed. In many cases, the silicon appears to be partially replaced by carbon. The existence of the silicides, $FeSi_2$, Fe_3Si_2 and Fe_5Si_2 , which have been described by other observers, is considered doubtful.

N. L.

Preparation of Uranium. By JULES ALOY (*Bull. Soc. Chim.*, 1901, [iii], 25, 344—346).—Small quantities of uranium may readily be obtained by heating a mixture of the oxide U_3O_8 with sugar carbon in the electric furnace, using a current of 150 amperes at 50—60 volts; the high current densities employed by Moissan are, therefore, not absolutely necessary. The oxide may also be reduced by heating to redness with magnesium or aluminium, but a better method, admitting of the ready separation of the uranium, consists in heating a mixture of the oxide UO_2 with carbon to dull redness and starting the reduction by adding a cartridge of magnesium and barium dioxide.

N. L.

Studies on Solutions of Tin Salts. I. Electrical Conductivity of Solutions of Stannous Chloride and Hydrochloric Acid. By STEWART W. YOUNG (*J. Amer. Chem. Soc.*, 1901, 23, 21—36. Compare Abstr., 1898, ii, 595).—Stannous chloride and hydrochloric acid form molecular complexes in solution, the formation of such complexes increasing with the concentration. In so far as reduction of electrical conductivity may be taken as a measure of such association, there is evidence of two distinct forms of association, one being considerably more sensitive to dilution than the other, that is, having a larger dissociation constant. Potassium chloride shows a greater power of association at large concentrations than does hydrochloric acid, and it appears that potassium iodide has a still greater influence in the direction of forming complexes in stannous chloride solutions. J. C. P.

Antimonic Acids. By A. E. DELACROIX (*Bull. Soc. Chim.*, 1900, [iii], 25, 288—289. Compare Abstr., 1900, ii, 145).—Antimonic hydroxide is obtained in a pulverulent form by dissolving 1 kilogram of antimony trichloride in a litre of hydrochloric acid, heating the solution to 100°, adding 250 c.c. of nitric acid, cooling, and adding water. It dissolves in warm water to form tetra-antimonic acid; a solution saturated at 70° contains 53.89 grams Sb_2O_5 per litre, and has a sp. gr. 1.0497. The existence of the following antimonates is indicated by neutralising triantimonic acid with alkalis under various conditions: $\text{K}_2\text{O}, 2\text{Sb}_2\text{O}_5$; $4\text{K}_2\text{O}, 5\text{Sb}_2\text{O}_5$; $\text{Li}_2\text{O}, \text{Sb}_2\text{O}_5$; $4\text{BaO}, 5\text{Sb}_2\text{O}_5$; $9\text{BaO}, 10\text{Sb}_2\text{O}_5$; $2\text{BaO}, 3\text{Sb}_2\text{O}_5$. N. L.

Basic Nitrates of Bismuth. By F. B. ALLAN (*Amer. Chem. J.*, 1901, 25, 307—315).—The basic nitrate, $\text{BiO} \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$, is readily obtained if nitric acid solutions of bismuth are poured into water at the ordinary temperature and the precipitate quickly removed. Even when the mother liquor is in equilibrium with more basic salts, the same compound is obtained, since, where the strong acid solution meets the water and the precipitate is formed, the concentration of the acid is high, and, even when the crystalline precipitate comes in contact with weaker acid, the action is too slow to produce any appreciable change in the course of a few hours.

At 21°, the salt $\text{Bi}_{12}\text{O}_{13}(\text{NO}_3)_{10} \cdot 9\text{H}_2\text{O}$ is in equilibrium with nitric acid solution from 0.03 to 0.32 *N*, and the salt $\text{BiO} \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$ with solutions from 0.425 to 0.72 *N*.

At 50°, the salt $\text{Bi}_4\text{O}_5(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ is in equilibrium with nitric acid solutions from 0.057 to 0.285 *N*, and the salt $\text{Bi}_{12}\text{O}_{13}(\text{NO}_2)_{10} \cdot 9\text{H}_2\text{O}$ with solutions from 0.285 to 0.466 *N*.

At 75°, the salt $\text{Bi}_4\text{O}_5(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ is in equilibrium with solutions from 0.109 to 0.314 *N*.

No basic nitrate containing a greater proportion of nitric anhydride than the salt $\text{Bi}_4\text{O}_5(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, and less than $\text{Bi}_{12}\text{O}_{13}(\text{NO}_3)_{10} \cdot 9\text{H}_2\text{O}$, exists at 50°, although at least two have been previously described.

J. J. S.

Presence of Platinum amongst the Characters of a Hieroglyphic Inscription. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 729—732).—One of the hieroglyphs on an Egyptian box,

found at Thebes and dating from the seventh century B.C., was found to consist mainly of platinum, which, however, from its resistance to the action of acids, was probably alloyed with iridium. C. H. B.

Mineralogical Chemistry.

Theories of the Origin of Petroleum. By CONSTANTIN KLEMENT (*Bull. Soc. Belge Geol.*, 1901 (for 1897), 11, *Proc.-Verb.*, 76—85).—A résumé is given of the various theories which have been proposed.

L. J. S.

Discovery and Occurrence of Minerals containing Rare Elements. By ADOLF ERIK NORDENSKIÖLD (*Quart. J. Geol. Soc.*, 1900, 56, 521—530).—A historical survey is given of the discovery and occurrence, especially in Scandinavia, of minerals (cerite, thorite, fergusonite, &c.) containing rare elements, and in which the new gases, helium, &c., have been found.

L. J. S.

Metalliferous Deposits of Canton Grisons. By CHR. TARNUZZER, GUSTAV NUSSBERGER, and P. LORENZ (*Jahresber. Naturf. Ges. Graubündens*, 1900, 43, 1—47).—Several analyses are given of ores, especially ores of iron.

L. J. S.

Chalcopyrite. By LEONARD P. MORGAN and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1901, 23, 107—109).—Chalcopyrite contains the whole of its iron in the ferrous state.

E. G.

Separation of Titaniferous Iron Ores in Basic Igneous Rocks. By JOHAN H. L. VOGT (*Chem. Centr.*, 1901, i, 473, 536; from *Zeit. Prakt. Geol.*, 1900, 370—382; 1901, 9—19).—The discussion of this problem is continued (this vol., ii, 63). Analyses have been made to determine which elements are concentrated with the titanium and which are not. Details are given of the method employed for the estimation of titanium.

L. J. S.

Canadian Minerals. By G. CHRISTIAN HOFFMANN (*Zeit. Kryst. Min.*, 1901, 34, 209—210; from *Ann. Rept. Geol. Survey Canada*, for 1898, 1900, 11, Part R).—The following mineral analyses by R. A. A. Johnston are given. Celestite: milk-white, translucent, radiated material forming a vein at Bagot, Renfrew Co., Ontario, gave the following results, corresponding with SrSO_4 , 85.63; BaSO_4 , 14.38 per cent.:

| SO_3 . | SrO . | BaO . | CaO . | Total. | Sp. gr. |
|-----------------|----------------|----------------|----------------|--------|---------|
| 42.09 | 48.30 | 9.44 | trace | 99.83 | 3.994 |

Hübnerite: brownish-black material with submetallic lustre, con-

choidal fracture, and a lamellar structure, occurs in quartz, associated with copper pyrites, and yellow hydrated mica, at Emerald, Inverness Co., Nova Scotia.

| WO ₃ . | MoO ₃ . | MnO. | FeO. | CaO. | MgO. | SiO ₂ . | Total. | Sp. gr. |
|-------------------|--------------------|-------|------|------|------|--------------------|--------|---------|
| 74.28 | trace | 22.73 | 0.47 | 0.02 | 0.86 | 1.33 | 99.69 | 6.975 |

Hydromagnesite: a large deposit of this occurs near "108, Mile House," on the Cariboo Road, British Columbia. Analysis of pure white material gave:

| CO ₂ . | MgO. | CaO. | Al ₂ O ₃ . | Fe ₂ O ₃ . | P ₂ O ₅ . | SiO ₂ . |
|---|-------|------|----------------------------------|----------------------------------|---------------------------------|--------------------|
| 37.03 | 43.71 | 0.10 | 0.02 | 0.04 | 0.30 | 0.38 |
| H ₂ O and some organic matter. | | | | Insol. | Total. | |
| 17.79 | | | | 1.53 | 100.90 | |

Natron: large quantities of this occur on the bed of the Goodenough lake, Lilloet district, British Columbia. Analysis of a transparent fragment gave the following results. On ignition the material loses 0.29 per cent. of carbon dioxide:

| Na ₂ O. | CO ₂ . | H ₂ O. | NH ₃ . | SO ₃ . | P ₂ O ₅ . | B ₂ O ₃ . |
|--------------------|-------------------|-------------------|--------------------|-------------------|---------------------------------|---------------------------------|
| 21.36 | 15.46 | 63.03 | little | 0.08 | 0.01 | trace |
| | | Cl. | SiO ₂ . | Total. | | |
| | | 0.01 | 0.01 | 99.96 | | |

Other mineral occurrences are mentioned.

L. J. S.

Glaucescence of Felspars. By CARLO VIOLA (*Zeit. Kryst. Min.*, 1901, **34**, 171—195).—The name glaucescence is applied to the blue schiller shown by certain felspars, as distinct from the multicoloured schiller shown by labradorite (labradorescence). The phenomenon is described and discussed in detail. One of the felspars examined is moonstone from Ceylon, of which the following analysis by E. H. Kraus is given:

| SiO ₂ . | Al ₂ O ₃ . | CaO. | K ₂ O. | Na ₂ O. | Ignition. | Total. |
|--------------------|----------------------------------|------|-------------------|--------------------|-----------|--------|
| 65.87 | 19.45 | 0.51 | 11.91 | 2.57 | 0.18 | 100.49 |

L. J. S.

Labradorite and Topaz from N.S. Wales: Estimation of Fluorine. By GEORGE HARKER (*Zeit. Kryst. Min.*, 1901, **34**, 213; from *J. and Proc. Roy. Soc. New South Wales*, 1899, **33**, 193—203; and *Chem. News*, 1900, **82**, 56—57, 64—66).—Analyses I and II are of fragments of labradorite from a basalt at Sandilands Mountain, New England. The material is colourless to brown; sp. gr. 2.70:

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | Na ₂ O. | K ₂ O. | MgO. | H ₂ O. | Total. |
|--------------------|----------------------------------|----------------------------------|------|--------------------|-------------------|--------|-------------------|--------|
| I. 55.05 | 30.15 | 10.32 | 5.11 | nil. | nil. | undet. | | 100.63 |
| II. 54.81 | 29.70 | 0.42 | 9.61 | undet. | 0.29 | 0.28 | 0.13 | — |

Analyses III and IV are of transparent, rolled fragments of topaz from Mudgee; V and VI of green topaz from New England; VII and VIII of topaz from Brazil.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | F. | H ₂ O (ignition). | H ₂ O (with PbO). | Total. |
|-------|--------------------|----------------------------------|----------------------------------|-------|------------------------------|------------------------------|--------|
| III. | 31·90 | 56·62 | — | 17·90 | 0·23 | 0·75 | 107·40 |
| IV. | 31·84 | 56·80 | — | 17·00 | 0·26 | 0·75 | 106·65 |
| V. | 31·73 | 55·62 | 0·12 | 16·30 | 0·37 | 1·07 | 105·21 |
| VI. | 31·92 | 55·43 | — | 15·92 | 0·39 | 1·07 | 104·73 |
| VII. | 31·95 | 54·52 | — | 14·62 | 0·23 | 2·12 | 103·44 |
| VIII. | 32·16 | 54·61 | — | 14·23 | 0·30 | 2·12 | 103·42 |

The author has tested the several methods for the estimation of fluorine, and obtained exact results only with that of Berzelius. When alumina is present the mineral is mixed with half its weight of silica before being fused with alkali carbonates, otherwise the results obtained for fluorine are too low, whilst those for silica and alumina are too high.

L. J. S.

[Mineral Analyses.] By M. KIŠPATIĆ (*Wiss. Mitth. Bosnien u. d. Herzegovina*, 1900, 7, 377—484).—The following mineral analyses are given in a petrographical paper on the crystalline rocks of the serpentine zone of Bosnia. I, Diopside from the chromite mine in the Iherzolite at Milakovac, Borja planina. II, Diopside, which forms with bronzite a rock in the Iherzolite at Pobilje. III, Bronzite from the same rock as the last. IV, Actinolite schist, composed only of actinolite, from near Kopalište. V, Meerschaum from the magnesite mines in the serpentine at Reljevac. Five analyses are also given of serpentine:

| | SiO ₂ . | Al ₂ O ₃ . | Cr ₂ O ₃ . | FeO. | CaO. | MgO. | Ign. | Total. |
|------|--------------------|----------------------------------|-------------------------------------|------|-------|-------|-------|--------|
| I. | 50·84 | 0·43 | trace | 7·18 | 21·49 | 16·54 | 4·23 | 100·71 |
| II. | 50·62 | 3·98 | trace | 7·20 | 19·39 | 15·76 | 3·20 | 100·15 |
| III. | 56·00 | 0·72 | — | 8·98 | 0·59 | 32·44 | 1·77 | 100·50 |
| IV. | 44·56 | 6·00 | — | 9·89 | 21·34 | 13·30 | 4·65 | 99·74 |
| V. | 61·09 | — | Fe ₂ O ₃ 2·59 | — | — | 25·87 | 10·47 | 100·02 |

L. J. S.

Limestones of New York and their Economic Value. By HEINRICH RIES (51st *Ann. Rept. N.Y. State Museum*, for 1897, 1899, ii, 355—467).—An account is given of the geological and geographical distribution of limestones in the State of New York, with details of the economic uses. Several analyses are given.

L. J. S.

A Diluvial Boulder of Nephrite in a Street Pavement at Breslau. By GEORG GÜRICH (*Centr. Min.*, 1901, 71—73).—A boulder of green stone in a street pavement at Breslau was shown by the microscopical examination of thin sections and the following analysis to consist of nephrite. It was, no doubt, brought to its present locality by the northern ice-sheet:

| SiO ₂ . | Al ₂ O ₃ . | FeO. | MgO. | CaO. | H ₂ O. | Sp gr. |
|--------------------|----------------------------------|------|------|------|-------------------|--------|
| 56·9 | 1·4 | 5·3 | 17·6 | 15·9 | 3·2 | 2·96 |

L. J. S.

Uralitised Diallage from the Ardennes. By CONSTANTIN KLEMENT (*Bull. Soc. Belge Geol.*, 1901 (for 1897), 11, *Proc.-Verb.*, 150—155).—The crystals in a rock from Recogne, which was described

in 1883 as a chiastolite rock, are now found, on a detailed examination, to be diallage altered to uralite. The excess of silica shown in the following analysis is due to inclusions of quartz in the crystals :

| SiO . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | CaO. |
|-------|----------------------------------|----------------------------------|-------------------|--------|-------|
| 62·26 | 8·89 | 2·55 | 5·37 | traces | 11·23 |
| | MgO. | Na ₂ O. | H ₂ O. | Total. | |
| | 7·51 | 0·20 | 3·65 | 101·66 | |

L. J. S.

Rocks from the Volcano of Etinde, Cameroons. By E. ESCH (*Sitz.-Ber. Akad. Wiss. Berlin*, 1901, 277—299 ; 400—417).—A petrographical description, with chemical analyses, is given of leucite, nepheline, and hainyne rocks from the volcano of Etinde. L. J. S.

Meteorite from Ceylon. By STANISLAS MEUNIER (*Compt. rend.*, 1901, 132, 501—503).—A description is given of a stone which fell near Mulletiwa in the province of Carnawelpattu, Ceylon, on April 13th, 1795. The structure is chondritic and of the montresite type. Sp. gr., 3·677. Analysis gave: nickel-iron, 17·25 ; silicates (mainly olivine) decomposed by hydrochloric acid, 41·22 ; undecomposed silicate (enstatite), 32·27 per cent. ; troilite, chromite, &c., are also present. The nickel-iron contains 8 per cent. of nickel. L. J. S.

The Red Rain at Palermo in March, 1901. By STANISLAS MEUNIER (*Compt. rend.*, 1901, 132, 894—896).—The author has examined a specimen, collected at Palermo, of the red rain which fell in Tunis, Sicily, and the neighbourhood of Naples on the night of March 9—10, 1901. It is a very fine pale red powder, which is harsh to the touch, scratches glass readily, and is highly charged with air, which it retains very tenaciously. It contains: water, 5·20 ; organic matter, 3·17 ; sand, 59·14 ; calcium carbonate, 23·91 ; clay, 8·58 = 100·00, but small quantities of chlorides, sulphates, and magnesium are also present. The sand consists mainly of angular fragments of quartz, and the substance contains a relatively high proportion of the skeletons of diatoms. The red rain is of the same general character as that observed on previous occasions, and there seems little doubt that it has been removed from the soil of the Sahara by violent atmospheric disturbances. C. H. B.

Thermal Water from Vals, Lugnez Valley. By GUSTAV NUSSBERGER (*Jahresber. Naturf. Ges. Graubündens*, 1900, 43, 67—68).—Analyses are given of the water which issues from the upper and from the lower part of the bore. The water is ferruginous and contains much gypsum. Temperature 25·2°. L. J. S.

Mineral Springs of Val Sinestra, Lower Engadine. By GUSTAV NUSSBERGER (*Jahresber. Naturf. Ges. Graubündens*, 1900, 43, 69—103).—Detailed analyses are given of waters from three springs, and earlier analyses are quoted for comparison. L. J. S.

Origin of Hot Sulphuretted Waters: Thiosilicates and Oxy-sulphides derived from Natural Silicates. By ARMAND GAUTIER (*Compt. rend.*, 1901, 132, 740—746).—When powdered granite is

treated with cold water, it yields about 1 gram per kilogram of sodium silicate and calcium sulphate, together with smaller quantities of other salts, but the solution contains no sulphides. If, however, the granite is heated with its own weight of water at 250—300° in sealed tubes free from air, a sulphuretted water is obtained identical in composition with many natural hot sulphuretted waters, but containing a larger quantity of alkali hydrosulphides. Like the natural waters, the solution thus obtained contains only minute quantities of potassium salts. All igneous rocks behave in the same way. Ferrous sulphide is not decomposed by water at 260—280° and the hydrogen sulphide is most probably produced by the action of the water on thiosilicates and oxysulphides, which, as the author has previously shown (Abstr., 1889, 212), are formed when reducing gases, such as are liberated when igneous rocks are heated (this vol., ii, 171) act, together with hydrogen sulphide or sulphur, on feldspars, kaolin, alumina, &c. Direct experiment shows that if albite is heated to bright redness in the gases liberated from granite at a high temperature, and is afterwards heated in water at 250°, it yields a sulphuretted and slightly alkaline solution, although no similar results are obtained with albite in its natural condition. Further, thiosilicates, when heated in chlorine, lose part of their sulphur in the form of chloride, and the author finds that when igneous rocks are heated in the gas, small quantities of sulphur chloride are obtained. The presence of the thiosilicates and oxysulphides in igneous rocks is therefore highly probable.

C. H. B.

Physiological Chemistry.

Influence of Certain Materials on the Quantity and Quality of Gastric Juice. By ALEX. HERZEN (*Pflüger's Archiv*, 1901, 84, 101—114).—After a summary of Pawlow's recent work ("Die Arbeit d. Verdauungsdrüsen," 1898), and Schiff's well-known older researches on peptogens, a number of experiments are described performed on dogs, which show that the amount and activity of gastric juice secreted do not necessarily vary together. Some materials (for example, dextrin) given as food are mainly peptogenic, whereas other substances (such as Liebig's extract) increase the flow of juice (safttreibend) without increasing markedly the amount of pepsin.

W. D. H.

Action of "Saccharin" on Gastric Digestion. By ALLYRE CHASSEVANT (*Compt. rend. Soc. Biol.*, 1901, 53, 206—207).—The addition of "saccharin" (benzoic sulphinide) to artificial gastric juice hinders its proteolytic activity, as tested by Mette's tubes. The following are the figures given :

| | Digestive power. |
|--|------------------|
| Gastric juice, control experiment | 100 |
| „ addition of 0·04 "saccharin" per cent... | 58 |
| „ „ 0·2 „ „ | 29 |
| „ „ 0·4 „ „ | 7 |

W. D. H.

Ferment acting on Salol in Various Organs. By P. NOBÉCOURT and PROSPER MERKLIN (*Compt. rend. Soc. Biol.*, 1901, **53**, 148—149).—The presence of a ferment which converts salol into salicylic acid is not peculiar to the pancreatic juice, but is found also in bile, the gastric and intestinal mucous membranes, the liver, spleen, suprarenal, kidney, lung, muscle, brain, blood-serum, human milk, the milk of the dog, but not of the cow, ass, or goat. The amount of activity varies considerably in the different cases. It is favoured by an alkaline, and inhibited by an acid, medium. It is possibly identical with lipase. W. D. H.

The Rôle of the Spleen in Trypsin Formation. By ALEX. HERZEN (*Pflüger's Archiv*, 1901, **84**, 115—129).—Schiff held strongly, on what appeared to him sufficient experimental evidence, that the spleen plays an important part in the formation of pancreatic juice, especially in so far as trypsin is concerned. The present author, with whom Schiff worked, has frequently laid these views before physiologists. The present paper is mainly a repetition of previous statements on the subject. The main idea is that the spleen forms an internal secretion, which contains an unknown substance having the property of converting protrypsin into trypsin. W. D. H.

Properties of Pancreatic Juice in Starving Animals. By ÉMILE WERTHEIMER (*Compt. rend. Soc. Biol.*, 1901, **53**, 139—141).—In a fasting animal, a flow of pancreatic juice can be excited by stimulation of the intestinal (especially the duodenal) canal. This juice acts rapidly on starch, but not on proteids. Pilocarpine, however, causes the formation of a juice which acts vigorously also on proteids. W. D. H.

Properties of Pancreatic Juice in Starving Animals. By LUCIEN CAMUS and EUGÈNE GLEY (*Compt. rend. Soc. Biol.*, 1901, **53**, 194—196).—The flow of pancreatic juice produced by duodenal irritation is more abundant, and contains less solid than that poured out after a dose of pilocarpine. After pilocarpine, even in a starving animal, the juice is strongly proteolytic and lipolytic. This confirms Wertheimer's experiments (see preceding abstract) and is strongly opposed to the Schiff-Herzen theory, which presupposes splenic activity to be necessary for the formation of trypsin. W. D. H.

Mechanism of Lipolytic Reactions. By MAURICE HANRIOT (*Compt. rend.*, 1901, **132**, 842—845. Compare this vol., ii, 175).—The hydrolysis of glyceryl esters by lipase, is most readily explained by supposing that this ferment is a weak base, which combines with the fatty acid to form a readily dissociated salt. The oxides of ferric iron and aluminium possess similar properties, forming unstable salts with the organic acids; they also promote the hydrolysis of glyceryl esters, but to an extent far less than that noticed when lipase is employed. Lipase may itself be an iron salt, serum always containing a small quantity of this element; the hydrolytic action is diminished by reducing the iron compound with zinc. On the other hand, the addition of a ferric salt to serum freed from lipase does not restore

the hydrolytic property of the solution. Hematogen, the ferruginous pigment of the egg, has strongly marked lipolytic properties.

G. T. M.

Amylolytic Ferment of the Liver. By PERMILLEUX (*Compt. rend. Soc. Biol.*, 1901, 53, 32—34). **Chloroformic Dialysis and Endo-cellular Ferments.** By A. DASTRE (*ibid.*, 34—35).—If a liver free from blood is exposed in a vacuum to chloroform vapour, a liquid is exuded which contains an amylolytic ferment. This ferment belongs to the class of *endo-cellular* enzymes, and by this term is distinguished from the amylolytic ferment produced by the pancreas which is *exo-cellular*. Some endo-cellular enzymes require severe measures to separate them from the cells, as in Buchner's work with yeast. In other cases, as the present, a comparatively simple method termed 'chloroformic dialysis' is sufficient for the purpose.

W. D. H.

Nuclein Metabolism. By OTTO LOEWI (*Chem. Centr.*, 1901, i, 585; from *Arch. exp. Path. Pharm.*, 45, 157. Compare Abstr., 1900, ii, 417).—From experiments on the author's person, it is found that the nuclein in the food is in part decomposed in the intestine; the phosphoric acid leaves the body in the fæces, and the nitrogenous part is absorbed. The main portion of the nuclein (except when pancreas nuclein is taken) is absorbed, the phosphoric acid remaining in organic union. Feeding on nuclein does not lessen the amount of urea excreted; the fall in urea noticed after feeding on thymus is due to the richness of that organ in extractives. The use of guanine in the form of nuclein increases the uric acid output considerably. Certain points in the work of Burian and Schur are criticised.

W. D. H.

Hæmolysis produced by Solanine. By E. HÉDON (*Compt. rend. Soc. Biol.*, 1901, 53, 227—229).—Acids prevent the destruction of blood corpuscles produced by salts of solanine. Bashford (*Arch. internat. pharmacodyn. et de thérapie*, 1901, 8, 101) considers this is due to acids preventing or lessening the liberation of solanine by dissociation of its salts. The present paper discusses the question raised.

W. D. H.

Estimation of Fat in Blood, and the Amount of Fat in Human Blood. By M. BÖNNINGER (*Chem. Centr.*, 1901, i, 583—584; from *Zeit. klin. Med.*, 42, 65—71).—Some of the discordant results of fat analysis in blood are due to method, and some to the fact that lipolysis occurs. Hoppe-Seyler's method of alcohol extraction gives good results for clinical purposes. In human blood, the percentage of fat is fairly constant (0.75—0.85). In nephritis and diabetes, it rises; in a case of cancer of the œsophagus it rose to 1.4. In ethereal extracts, cholesterol esters are found in addition to neutral fats and lecithin.

W. D. H.

A Method of Distinguishing Varieties of Blood. By UHLENHUTH (*Chem. Centr.*, 1901, i, 584; from *Deutsch. med. Woch.*, 27, No. 6).—The important forensic question of distinguishing human blood from the blood of other animals is the main point of the investigation. Eighteen different kinds of animals were used, and the follow-

ing general rule discovered. If a rabbit receives a weekly intraperitoneal injection of 10 c.c. of the defibrinated blood from an animal of another species, at the end of a month the blood serum of that rabbit is rendered cloudy by the addition of a little blood diluted with water (1 : 100) of that animal. Thus, if a rabbit is treated with human blood, the rabbit's serum is rendered cloudy by the addition of human blood, but not by the blood of any other animal. W. D. H.

Electromotive Phenomena of Resting Frog's Muscle. By MAX OKER-BLOM (*Pflüger's Archiv*, 1901, 84, 191—259. Compare Abstr., 1900, ii, 290, 356, 607).—A continuation of the author's researches on the physico-chemical properties of animal tissues and fluids. A curarised sartorius of the frog, which is electrically streamless, was taken as the subject of the experiments. The addition of water produces negativity, followed later by positivity. Extremely dilute solutions of potassium chloride produce the same effect, but more rapidly. If the concentration of the salt is increased, the second phase disappears. These facts are all stated to be easily explicable on physical grounds such as ionic action between the contractile substance of the muscular fibres and the membranes that enclose them.

W. D. H.

Glycogen in Animal Organs. By G. MEILLÈRE and LÉPER (*Compt. rend. Soc. Biol.*, 1901, 53, 153—155).—The amount of glycogen was estimated in a number of organs, and the chemical analyses compared with the histological appearances; the histological method employed was fixation with alcohol and coloration with iodised gum (Ehrlich-Brault). The following figures may be quoted; they give the amount of glycogen in parts per 1000 of the organ or tissue mentioned: rabbit's liver, 8; rat's liver, 15; muscles of horse, 4 to 5; heart muscle, 2.5. The glycogen of heart muscle is not stable, and rapidly disappears. No glycogen was found in pancreas, spleen, lung, ovary, testis, &c. White blood corpuscles contain variable traces.

W. D. H.

Elimination of Cacodylic Acid from the Organism. By LÉONCE BARTHE and R. PÉRY (*J. Pharm.*, 1901, [vi], 13, 209—214).—See this vol., ii, 364.

Iron of Normal Urine. By FRANCESCO NICOLA (*Chem. Centr.*, 1901, i, 584—585; from *Estr. Giorn. Accad. Med. Torino*, 6).—Iron in the urine was estimated by the methods of Hamburger (*Zeit. physiol. Chem.*, 2, 195; 4, 249) and of Lapicque (Abstr., 1895, ii, 407). The amount *per diem* is fairly constant in human urine. It averages 0.00075 gram per 1000. The deeper coloured urine of the night contains more than that of the morning or afternoon; there is, however, no necessary correspondence between iron and urinary pigment.

W. D. H.

Estimation of Iron in Normal and Pathological Human Urine. By PAUL HOFFMANN (*Zeit. anal. Chem.*, 1901, 40, 73—82).—The author has made nine estimations of iron in normal urine, with results ranging from 0.49 to 1.7 milligrams (average 1.09) in

the day's excretion. The method of preparing the urine for the estimation was varied, some specimens being incinerated as described by Jolles (Abstr., 1897, ii, 286), whilst in others the organic matter was destroyed by boiling down with nitric acid and heating with ammonium nitrate and sulphuric acid (Abstr., 1899, ii, 814). The latter method is the more convenient, and preliminary experiments showed that both methods gave the same result. In no case was less than 500 c.c. of urine employed. The iron was always precipitated with ammonium sulphide, the ferrous sulphide redissolved by fusion with potassium anhydrosulphate, the solution reduced by zinc in an atmosphere of carbon dioxide, and titrated with permanganate, correcting for the iron in the zinc. The much higher results obtained by Jolles seem incapable of explanation, but the still higher ones of Müller and Hamburger were probably due to experimental errors. The average in three cases of leucæmia was 1.37 mg. (1.03—1.09), whilst six specimens of diabetic urine gave results ranging from 1.83 to 5.88 mg., and a single case gave 22.02 mg. The urine of a phthisical subject, amounting to only 230 c.c. in 2 days, contained only 0.47 mg. per day. M. J. S.

Respiratory Exchange in Tuberculosis. By ALBERT ROBIN and MAURICE BINET (*Compt. rend.*, 1901, 132, 709—711).—Although the amount of air breathed is less in a phthisical person than in a healthy one, the respiratory exchange is more active. The same is true in cases of tuberculosis of the testis, pleura, and lymph glands, but not in that of tubercular peritonitis, meningitis, and lupus. Examination of the respiratory metabolism is believed to be of diagnostic value in cases of doubtful phthisis. Increase of respiratory activity is stated also to occur in descendants of phthisical parents, before the invasion of the bacillus, and the condition is believed to be favourable to the growth of the bacillus. W. D. H.

Toxic Action of Electrolytes on Fishes. By LOUIS KAHLENBERG and HUGO F. MEHL (*J. Physical Chem.*, 1901, 5, 113—132).—The species of fish used were yellow perch, rock-bass, dace, and brook-trout. These were immersed in various dilute solutions of electrolytes and the time noted until the fish lost control of its motion and turned over on its back. The vitality of the fishes is in the order given.

The experiments with acids and alkalis indicate that the dissociation theory is not capable of explaining the action of the various solutions. Thus, hydrochloric and nitric acids in solution of greater dilution than $N/100$ have apparently the same toxic action, but sulphuric acid solutions of equivalent normality are somewhat less virulent, although complete dissociation may be assumed for so dilute solutions. $N/50$ acetic acid is appreciably more virulent than $N/1000$ hydrochloric acid, although it contains fewer hydrogen ions. The toxicity of potassium hydroxide solution changes so slightly with dilution that the action is probably not due to hydroxyl ions.

Silver nitrate and sulphate at equivalent dilution have almost the same action; these are extremely poisonous, more so even than potassium cyanide or mercuric chloride. Other salts have also been examined.

The length, weight, and *post mortem* examination of the fishes are given. J. McC.

Pharmacological Researches on some Cyanopyridone Derivatives. By A. DERIU (*Chem. Centr.*, 1901, i, 582; from *Giorn. Real. Accad. di Medicina Torino*, 1900, 6).—The author has investigated the action on dogs, rabbits, and cats of the following compounds: 3-cyano-2-oxy-4:6-dimethylpyridine; 3-cyano-2-oxy-4:5:6-trimethylpyridine; 3-cyano-2-oxy-1:4:6-trimethylpyridine; 3-cyano-2-oxy-1:4:5:6-tetramethylpyridine; and 3-cyano-2-oxy-1:4:6-trimethylpyridine. All these substances produce a rapid action on the nervous system, causing intense convulsions and marked epileptic attacks together with increased flow of saliva and myosis; their poisonous action is, however, slight (compare Sabbatani, 1900, ii, 94). Conclusions are drawn with regard to the influence of an increase of molecular weight and of the number of methyl groups in the molecule on the intensity of the poisonous action. T. H. P.

Chemistry of Vegetable Physiology and Agriculture.

Production of Acetylmethylcarbinol by *Bacillus Tartricus*. By LÉON GRIMBERT (*Compt. rend.*, 1901, 1, 706—708).—A 5 per cent. solution of dextrose or sucrose containing traces of peptone and calcium carbonate is treated for 15 days with a pure culture of *Bacillus tartricus* at 37° and then filtered and distilled; the distillate contains a compound reducing Fehling's solution even in the cold which is identified as acetylmethylcarbinol by its osazone and osotetrazone (von Pechmann, Abstr., 1888, 1287). These sugars yield about 4 per cent. of this compound, whilst lactose and mannitol furnish smaller quantities; dextrin, glycerol, and calcium tartrate do not, under these conditions, give rise to any osazone. Negative results were obtained on substituting *B. coli*, Eberth's bacillus, and Friedländer's pneumobacillus for *B. tartricus* in the preceding experiment. G. T. M.

Influence of Phosphates on the Fermentative Action of Yeast Extract; Complex Phosphoric Acids and the Rôle of Phosphoric Acid in Animated Nature. By AUGUSTIN WRÓBLEWSKI (*Bull. Acad. Sci. Cracow*, 1900, 407—428. Compare Abstr., 1900, ii, 157).—The experiments were carried out as in the previous research (*loc. cit.*), using the extract from a pure culture of yeast. It is found that addition of 1 per cent. of sodium chloride, magnesium sulphate, or potassium nitrate reduces the fermentation, and 2½ per cent. entirely arrests it, whilst even 0·3 per cent. of sodium sulphate is sufficient to unfavourably affect the amount of fermentation. Dibasic phosphates (Na_2HPO_4) and monobasic phosphates (NaH_2PO_4) increase by three or four times the fermenting power of the extract. The former has an optimum effect at a concentration of 1·25, the latter at a concentration of 1 per cent. A mixture of these phosphates has

still a greater augmentative action. Four per cent. of phosphates produces a precipitate and stops fermentation. Acids and alkalis both arrest fermentation when they are present in sufficient quantity to produce a precipitate. Acids precipitate proteids, alkalis the phosphates always present in the extract. Addition of phosphates renders necessary a markedly greater quantity of sodium hydroxide either to reduce or arrest fermentation. Thus in the natural extract 0.1 per cent. of sodium hydroxide brings about a reduction, and 0.2 per cent. the arrest of fermentation; in the presence of phosphates, 0.5 per cent. of the alkali only intensifies the action of the extract, whilst 1 per cent. is required to stop it. Similarly, 0.3 per cent. of hydrochloric acid increases the fermentation, when phosphates have been added, a quantity which would completely destroy the activity of the natural extract.

The author believes that the function of phosphates in the yeast extract and in the yeast plant itself is to maintain the "double reaction" and preserve the active protoplasm of the cell from the injurious action of alkalis or acids, which may develop in the various chemical processes taking place in the living organism.

In the remainder of the paper the author discusses other functions of phosphoric acid in organisms, and draws attention to its capability of forming soluble compounds with various complex organic substances. There is evidence for the existence of such compounds in many liquids of organic origin, as yeast extract, whey, muscle extract, &c.

K. J. P. O.

Reduction of Nitrates in Presence of Farmyard Manure. By J. P. STREET (*Exper. Stat. Record*, 1900, 12, 321—322; from *New Jersey Stat. Rep.*, 1899, 86—96).—Fresh cow dung (about 30 grams) with (1) sodium nitrate, 1.25 gram; (2) ammonium sulphate, 1 gram; (3) dried blood, 1.5 gram, with or without gypsum, acid phosphate, kainite, sulphur (each 0.2 gram), and carbon disulphide (20 c.c.) was diluted to 300 c.c. with water, and kept in open flasks for a month at about 20°. The flasks were occasionally shaken. In one set of experiments, nitric nitrogen was determined at intervals of 7, 14, and 24 days, the second set being kept undisturbed the whole time.

In the mixture of dung and sodium nitrate, denitrification was complete in 24 days; the same mixture, with addition of gypsum, acid phosphate, kainite, and sulphur required 27, 27, 16, and 23 days respectively for complete denitrification. In presence of carbon disulphide, the mixture lost only 9.6 per cent. of its nitrate in 24 days.

In the mixture containing ammonium sulphate, the greatest loss amounted to 4.1 per cent. (with acid phosphate); with kainite and gypsum, there were slight gains.

In the second set of experiments, similar results were obtained with sodium nitrate. In the case of ammonium sulphate, there was always a considerable gain in soluble organic nitrogen (especially under the influence of sulphur and carbon disulphide); the amount of insoluble inorganic nitrogen also increased, most with sulphate, and least with carbon disulphide.

Free ammonia was formed in considerable quantity, especially in the ammonium sulphate and kainite experiments. In the case of dried blood, all the nitrate and combined ammonia were lost.

Kainite seems to have a strong influence in liberating ammonia, whilst carbon disulphide has a retarding effect. N. H. J. M.

Chemical Changes in the Germination of Seeds of *Vicia Faba*. By I. SHULOFF (*Exper. Stat. Record*, 1900, 11, 749; from *Izv. Moscow Selsk. Khoz. Inst.*, 1899, 5, 192—202).—The results of experiments with seedlings, 10 days old, showed that whilst the distribution of asparagine is fairly uniform, the other amino-compounds occur to a much greater extent in the cotyledons than in the stalks. With regard to peas, Lokot found that there was no concentration of asparagine in any particular part of the plant, and that the concentration of the other amides varied greatly. N. H. J. M.

Germination of Seeds as affected by certain Chemical Manures. By G. H. HICKS (*Exper. Stat. Record*, 1900, 12, 347—348; from *U.S. Dept. Agr. Div. Bot. Bul.*, 24, 15).—Experiments were made on the effect of sodium nitrate, potassium chloride, bone black, oyster shell lime, and a mixed manure (bone black, potassium chloride, and sodium nitrate) on the germination of wheat, lettuce, radish, and crimson clover. In many, if not in most, cases, the manures acted injuriously on the sprout after it had passed through the seed coats.

Potassium chloride and sodium nitrate are very detrimental in strengths of 1 per cent. Phosphoric acid and lime manures are much less injurious, and may be harmless if not employed in excess.

Commercial manures should not be brought into direct contact with germinating seeds.

The effect of chemicals on seeds before planting is no index of the effect produced by the same chemicals in the soil. Injury by chemical manures is due to their action on the young sprouts; the seeds themselves are only slightly injured, or are not injured at all.

It is very improbable that germination is benefited by the nitrogen, potassium, calcium, and phosphoric acid applied as manures. N. H. J. M.

Influence of Distance on the Growth and Composition of Plants. By CONRAD VON SEELHORST and PANAOVIC (*Exper. Stat. Record*, 1900, 12, 132; from *J. Landw.*, 1899, 47, 379—389).—Oats and spring wheat were grown in pots containing one, five, and eight plants. Of the different constituents, nitrogen was the most influenced. Taking the amount of nitrogen in oats, 1 plant per pot, as 100, the amounts were 80.5 and 70.1 per cent. when five and eight plants respectively were grown in one pot. The alteration in the total ash and ash constituents, although very marked, was not so great.

The nutritive value of the plants grown five and eight in a pot was only 85.42 and 76.91 per cent. as much as that of plants grown one in a pot. In accordance with what is usually observed, the relation of straw to grain increased as the distance between the plants was decreased. N. H. J. M.

Composition of Rye Grain at Different Stages of Ripeness. By N. K. NEDOKUCHAEFF (*Exper. Stat. Record*, 1900, 11, 636; from *Izv. Moscow Selsk. Khoz. Inst.*, 1899, 5, 212—224).—Rye grain, which was analysed at intervals of five days, beginning with the end of the period of flowering and ending with yellow ripeness, was found to accumulate carbohydrates, the soluble forms being rendered insoluble. There was also an increase of proteids and a decrease of other nitrogenous compounds. The relative amount of nitrogen as asparagine as compared with total nitrogen remained constant. N. H. J. M.

Influence of Anæsthetics on the Respiration of Plants. By N. MORKOWIN (*Exper. Stat. Record*, 1900, 12, 112—113; from *Rev. Gén. Bot.*, 1899, 11, 289—303).—Etiolated leaves and leaf buds of *Vicia faba* and *Lupinus luteus*, green leaves of *Ficus elastica* and *Phylodendron*, and embryos of sprouted wheat were subjected to the action of alcohol, ether, morphine hydrochloride, and solanine hydrochloride, in a Pettenkofer apparatus.

The results, in opposition to those of Bonnier and Mangin (*Ann. Sci. Nat.*, 1886, [vii], p. 5), showed that when the exposure to anæsthetics is prolonged for many hours, or even for several days, the intensity of respiration is considerably increased—by alcohol $1\frac{1}{2}$ times and by ether more than twice, in the case of *Vicia faba*. Morphine hydrochloride had no effect when the amount was 1:2000, but with 1:500 the respiration was increased $1\frac{1}{2}$ times.

In general, respiration was increased both in etiolated and in green plants. Alcohol (5 per cent.) checked the production of chlorophyll and the growth of the wheat germ. The diminution in respiration, in the case of plantlets, was in proportion to their growth.

N. H. J. M.

Presence of Copper in Plants and the Amount they may contain. By EDOUARD HECKEL (*Exper. Stat. Record*, 1900, 11, 1012—1013; from *Bul. Soc. Bot. France*, 1899, 46, 42—43).—Analyses of *Polycarpæa spirostylis* are given showing that one sample contained 30 mg. of copper per 1000 grams of dry matter, whilst other plants, growing in soil very rich in copper, contained as much as 500 mg. per kilogram. In Australia, the presence of *Polycarpæa* is thought to be an indication of copper in the soil. The ash of seeds of *Quassia gabonensis* was found to contain 0.698 per cent. of copper; the ash of the seeds, without the seed coat, contained only 0.254 per cent.

Viola calaminaria is said to contain considerable quantities of zinc, and the presence of the plant usually indicates zinc in the soil.

N. H. J. M.

Photosynthesis and the Coloration of Plants. By ED. GRIFFON (*Exper. Stat. Record*, 1900, 11, 1011—1012; from *Ann. Sci. Nat. Bot.*, 1899, [viii], 10, 1—123).—The deep green leaves of cereals, lettuce, begonias, and fuchsias possess a greater assimilative energy than the light green leaves, but the reverse holds good in the case of peaches, plums, cannas, and chrysanthemums. Red beets, purple filberts, purple sycamore, cannas and arums assimilated less than the

varieties with dark green leaves, whilst in the case of red atriplex and beech, which have the colouring matter in the epidermis, and the purple barberry, the colouring matter of which is in the palisade, assimilation was equal to that of the similar plants rich in chlorophyll.

Limodorum arbovitum, a plant with highly coloured foliage and containing a good deal of chlorophyll, seems to be unable to utilise carbon dioxide. The addition of copper salts to nutritive solutions (1 : 10000 or 1 : 20000) attacks the roots of plants and retards growth; at the same time, the colour of the chloroleucites is increased and the intensity of the colour of the plant and the assimilative energy are materially increased.

Sodium chloride is unfavourable to chlorophyll production, and causes plants to acquire a characteristic greenish-yellow or pale green colour; the mesophyll of the leaf is thickened.

Excess of lime often results in chlorosis. In the case of pears and grapes, the photosynthesis is reduced to about one-fifth or one-sixth of that of normal leaves.

N. H. J. M.

Aldehyde in Green Leaves. By JOHANN REINKE and E. BRAUN-MÜLLER (*Exper. Stat. Record*, 1900, 11, 710; from *Ber. deut. bot. Ges.*, 1899, 17, 7—12, and *J. Roy. Micros. Soc.*, 1899, 499).—The results of a number of experiments made with various plants indicated that the amount of aldehyde decreases in absence of light. The conclusion is drawn that aldehyde is not the first product of assimilation.

N. H. J. M.

Hydrocyanic Acid in Plants. By MARCO SOAVE (*Exper. Stat. Record*, 1901, 12, 518; from *Nuov. Giorn. Bot. Ital.*, 1899, 6, 219—238, and *J. Roy. Micros. Soc.*, 1900, 343).—The results of experiments with bitter almonds and *Pangium edule* indicated that cyanogen compounds in plants are transitional substances which furnish the plant with nitrogenous food. From the time the seeds begin to swell, the bitter almond contains no hydrogen cyanide so long as the embryo is dormant. Hydrocyanic acid only appears when germination begins, and then only in the stem. Sweet almonds are said not to contain amygdalin.

N. H. J. M.

Mode of Formation of Asparagine in Plants. By ERNST SCHULZE (*Bied. Centr.*, 1901, 30, 106—108; from *Landw. Jahrb.*, 27, 503—516. Compare this vol., ii, 184).—The decomposition of proteids during germination probably always results in the production of leucine, aminovaleric acid, tyrosine, phenylalanine, and arginine; it is not at all improbable that asparagine and glutamine are directly formed to some extent. Most of the nitrogenous decomposition products break up further, leaving a residue (? ammonia) which is utilised in the synthesis of asparagine and glutamine.

Asparagine is not only produced during germination, but also at subsequent periods, as, for instance, during the development of the leaf buds. It is not known whether the changes are similar to those which take place during germination; but there is no evidence to the contrary.

Asparagine also occurs in the roots of plants, sometimes in considerable quantity; amino-acids and other soluble crystallisable nitrogen

compounds generally accompany it. It is generally supposed that this asparagine is produced synthetically from inorganic nitrogen compounds acquired from the soil. Assuming that, in germination, asparagine is produced from ammonia, its mode of formation in germinating seeds would be the same as in roots.

N. H. J. M.

Synthesis of Proteids. By WILHELM PALLADIN (*Exper. Stat. Record*, 1900, 12, 310—311; from *J. Roy. Micros. Soc.*, 1900, 223. Compare Abstr., 1890, ii, 612).—Besides the intermediate products of the primary synthesis of proteids, there are products of the decomposition of proteids, intermediate products of the regeneration of the decomposition products, and various special decomposition products of the proteids. Decomposition of proteids only takes place in growing organs.

Ulva lactuca and *Enteromorpha intestinalis* were found to contain asparagine, but not tyrosine; the first stage in the primary synthesis of proteid cannot be tyrosine, which, like asparagine, is thought to be a simple product of decomposition of proteid. Neither asparagine nor tyrosine was found in *Salicornia herbacea* or in the (August) leaves of *Dahlia variabilis*. Leaves of *Robinia pseudacacia* contained small amounts of asparagine, but no tyrosine.

N. H. J. M.

Influence of Carbohydrates on the Production of Proteids in Plants. By ERNST SCHULZE (*Bied. Centr.*, 1901, 30, 108—109; from *Landw. Jahrb.*, 27, 516—520).—In the germination of *Lupinus luteus* a considerable decomposition of proteid takes place. Most of the products are subsequently converted into asparagine, which accumulates in large amount, owing to the small quantity of glucose present being insufficient to enable it to be completely transformed into proteids. When the seedlings have been kept for some time in darkness and are exposed to light, a portion of the glucose produced is available for the regeneration of proteids, but inasmuch as there is a renewed production of asparagine from other products of the decomposition of proteids, there is an increase in the asparagine as well as in the proteids.

N. H. J. M.

Constituents of Jamaica Dog-wood. By PAUL C. FREER and A. M. CLOVER (*Pharm. Arch.*, 1901, 4, 21—28).—From the powdered bark of Jamaica dog-wood (*Piscidia erythrina*) water extracts the calcium salt of *piscidic acid*, $C_9H_8O(OH)_2(CO_2H)_2$, which was purified by means of its insoluble lead salt. This acid melts at 182—185°, its *ethyl hydrogen* ester at 207—208°, its *dianilide* at 196°, and its *diacetyl* derivative at 149—151°; in aqueous solution, bromine converts it into a *substance* melting at 234—236°, possibly a dibromo-additive product.

Chloroform extracts a number of substances from the bark. If the extract is diluted with ether, washed with aqueous potassium hydroxide, evaporated, the residue washed with boiling light petroleum, and then covered with ether, two *substances* crystallise out. One, $C_{21}H_{14}O_5(OMe)_2$, melts at 201°, and yields products, $C_{22}H_{20}O_8$ (yellow), and $C_{22}H_{20}O_7$, melting at 159° and 136°, when heated with dilute and strong methyl alcoholic potassium hydroxide respectively. The other, $C_{20}H_{12}O_4(OMe)_2$, is yellow and melts at 216°. Hart's piscidin (Abstr.,

1884, 332) is a mixture of these two substances, and in reality is physiologically inert. Addition of light petroleum to the ethereal mother liquor of the crystals just described precipitates a *substance*, probably $C_{25}H_{22}O_7$, melting at 159° . On evaporation of the residual liquid, a *substance* melting at $50-80^\circ$ is left, probably a glucoside; when heated with slightly acidified alcohol, it yields some of the substance melting at 216° . A fifth *substance*, $C_{20}H_{20}O_5(OH)_2$, insoluble in light petroleum and melting at $150-155^\circ$, is also described as obtained from the chloroform extract; it forms a *diacetyl* derivative melting at 183° , and, when treated with potassium hydroxide and methyl iodide, a substance melting at $141-142^\circ$, described as probably a *dimethyl* derivative, although the formula $C_{20}H_{20}O_6$ is assigned to it. The substance itself is hydrolysed to a *product*, $C_{18}H_{14}O_4(OH)_2$, which melts at 275° , and forms a *diacetyl* derivative melting at $177-178^\circ$.

C. F. B.

Samadera Indica. By J. L. B. VAN DER MARCK (*Arch. Pharm.*, 1901, 239, 96-113).—A morphological description of the drug is given first. Then follows an account of the chemical investigation, for the details of which the original paper must be consulted. Most of the substances isolated were obtained in very small amount, often only a few hundredths of a gram from several kilograms of material. From the seeds were obtained:—(1) A fatty oil, forming 63 per cent. of the whole, and consisting of triolein 88, tripalmitin 8, and tristearin 4 per cent.; (2) a proteid, soluble in alcohol and in water, and containing 18 per cent. of nitrogen; (3) sucrose; (4) a sugar that reduces Fehling's solution directly; (5) inositol; (6) a crystalline bitter-substance. From the bark:—(1) The same bitter-substance as from the seeds; (2) a crystalline bitter-substance crystallising in yellow plates, probably an anthraquinone derivative; (3) a tannic acid belonging to the group of the phloroglucotannoids; (4) ellagotannic acid; (5) a tannic acid closely resembling tannin; (6) a large amount of inorganic salts. From the wood:—(1) A bitter-substance crystallising in yellow, rhombic prisms; (2) a bitter-substance very closely allied to quassin.

The bitter-substance that occurs in both seeds and barks crystallises in monoclinic plates, melts at 255° , and decomposes at 260° , and has $n_D^{20} 1.624$ and $[\alpha]_D^{20} +250^\circ$. It contains no water of crystallisation, and has the composition $C_{29}H_{34}O_{17}$. With phenylhydrazine, it yields a yellowish, crystalline substance, melting at 214° ; no methoxyl or ethoxyl group is present. It gives a violet coloration with strong sulphuric acid, and has a poisonous action on frogs, less so on guinea-pigs and rabbits. Most probably it is identical with the samaderin of Rost van Tonningen.

C. F. B.

Some Physiological Effects of Hydrogen Cyanide on Plants.

By W. G. JOHNSON (*Exper. Stat. Record*, 1900, 11, 1009-1010; from *Sci. Amer. Sup.*, 1899, 48, No. 1249, 20026-20027).—Hydrogen cyanide seems to be most injurious to foliage during sunshiny days, late in the autumn, between 9 a.m. and 4 p.m.; at other hours, even in sunshine, the leaves were little affected, and no injury

takes place at night. Dormant leaves of fruit trees were not injured by 0.2 gram of hydrogen cyanide per cubic foot.

Apple and pear trees remain practically uninjured by the strongest applications; plum trees are more susceptible, being injured by 0.65 gram of hydrogen cyanide per cubic foot. Peach trees, well matured, are injured by 0.5 gram, whilst low grade peach trees are killed when more than 0.18 gram is present. N. H. J. M.

Sensibility of Higher Plants to very Feeble Amounts of Toxic Substances. By HENRI COUPIN (*Compt. rend.*, 1901, 132, 645—647. Compare Abstr., 1899, ii, 118 and 242; 1900, ii, 236 and 363; also Dehérain and Demoussy, this vol., ii, 266).—The toxic effect of various salts was determined by observing the length of roots of wheat plants after 15 days of growth in the various solutions, as compared with the roots obtained in pure distilled water (30 cm.). The following amounts of salts were found to be toxic :

| | | | | | |
|---|-------------|--|---------|---|--------|
| CuSO ₄ | 1/700000000 | K ₂ Mn ₂ O ₈ .. | 1/15000 | Ba(NO ₃) ₂ .. | 1/4200 |
| HgCl ₂ | 1/300000000 | Mn(NO ₃) ₂ .. | 1/13000 | Li ₂ SO ₄ | 1/4000 |
| CdCl ₂ | 1/100000000 | LiCl | 1/12000 | NaOAc.... | 1/2000 |
| Ag ₂ SO ₄ | 1/2000000 | Al ₂ Cl ₆ | 1/10000 | Mg(OAc) ₂ . | 1/2000 |
| AgNO ₃ ... | 1/1000000 | MgI ₂ | 1/10000 | Na ₂ B ₄ O ₇ ... | 1/1000 |
| PdCl ₂ | 1/500000 | BaCl ₂ | 1/10000 | Ba(OAc) ₂ . | 1/1000 |
| Pb(NO ₃) ₂ .. | 1/100000 | CaI ₂ | 1/10000 | MnCl ₂ | 1/1000 |
| Al ₂ (SO ₄) ₃ ... | 1/500000 | Sr(NO ₃) ₂ .. | 1/6000 | CnBr ₂ | 1/400 |
| ZnSO ₄ | 1/40000 | LiNO ₃ | 1/5000 | CaCl ₂ | 1/260 |

The above amounts do not kill the plants, but injure the roots. Metallic mercury under water had no effect. The vapour emitted by mercury in air (not covered by water) is known to be injurious to vegetation (compare this vol., ii, 269). N. H. J. M.

Forcing Plants with Ether. By J. FISCHER (*Exper. Stat. Record*, 1900, 12, 243—244; from *Amer. Gard.*, 1900, 21, 358—360 and 372—373).—Treatment with ether is almost without action during the first and second portions of the resting period of plants; treatment during the last portion of the resting period (from the end of October to the end of December in the case of lilac) has a very stimulating effect. Shrubs may in this manner be forced 3—6 weeks earlier than by the usual methods. Etherised tulips were 8—12 days earlier than those without the treatment, but they did not hold the bloom so well. In the case of bulbs, growth is retarded if they are subjected to the action of ether before roots are formed. The beech was considerably retarded by ether. The colour of lilac was weaker in the case of plants treated with ether than in plants grown under ordinary conditions.

In the case of shrubs, the amount of ether employed was 1½ oz. to 40 gallons of air in the vapour-proof chamber.

Well developed flowers and improved colours were obtained by exposing plants which have been treated with ether to full light at temperatures from 50—54° F. (lilac) to 62—72° F. (Marly Rouge). N. H. J. M.

Variation in the Amounts of Gluten in Wheat. By LÉO VIGNON and F. COUTOURIER (*Compt. rend.*, 1901, 132, 791—794).—Different

varieties of wheat were grown on small plots (10 sq. m.) manured with the same amounts of phosphatic and potassium manures and different amounts of nitrogenous manures (35, 55, and 75 kilos. per hectare). The results show that the percentage of gluten increased with the amount of nitrogen applied. The increase was slow, and it is probable that in practice a limit would soon be reached.

Similar experiments with phosphoric acid showed a diminution in the amount of nitrogen when the phosphoric acid was increased from 75 to 150 and 225 kilos. per hectare. Millon found (*Compt. rend.*, 1854, 38, 95) that wheat grown in 1848 in the north of France contained 10.23 to 13.02 per cent. of gluten. At the present time, the percentage of gluten is 8.96 to 10.62. This diminution is attributed, not to loss of nitrogen in the soil, but to the large amounts of phosphatic manures which have been employed. N. H. J. M.

Analyses of Norwegian Barley. By FR. H. WERENSKIÖLD (*Bied. Centr.*, 1901, 30, 111—113; from *Tidsskr. Norsk. Landbr.*, 1900, 7, 68—74, and 109—114).—A number of results of analyses of Norwegian barley are given. On the whole, the results are considered satisfactory as regards the prospect of the production of malt-barley in Norway. N. H. J. M.

Sunflower Plant. By HARVEY W. WILEY (*U.S. Dept. Agr. Div. of Chem. Bul.*, 60, 1901, pp. 31. Compare *Ann. Rep. New York Agr. Expt. Stat.*, 2, 1883; *Ann. Rep. Maine Agr. Expt. Stat. for 1895*; and *Ann. Rep. Vermont Agr. Expt. Stat.*, 1893).—The first portions of the paper deal with the botanical description, medicinal uses, and the cultivation of the sunflower. The composition of the different parts of the plant is as follows:

| | Water. | Ether extract. | Crude fibre. | Proteid. | Carbo- hydrates. | Ash. |
|--|--------|-------------------|-----------------|----------|---------------------|-------|
| 1. Seeds | 4.43 | 27.08 | 29.17 | 14.97 | 20.94 | 3.41 |
| 2. Stems..... | 8.79 | 1.83 | 43.30 | 4.47 | 32.49 | 9.12 |
| 3. Leaves | 12.51 | 4.09 | 13.16 | 10.15 | 38.83 | 21.26 |
| 4. Heads, without seeds and husks | 7.40 | 5.07 | 18.44 | 9.91 | 39.79 | 19.39 |
| 5. Husks | 8.32 | 5.23 | 17.74 | 6.13 | 51.50 | 11.08 |
| 6. Kernels | 4.89 | 45.21 | 2.67 | 26.85 | 16.06 | 4.32 |
| 7. Seed shells | 6.16 | 1.67 | 63.75 | 3.00 | 23.22 | 2.20 |

The ash of the various parts had the following composition:

| | K ₂ O. | Na ₂ O. | CaO. | MgO. | Fe ₂ O ₃ . | P ₂ O ₅ . | SO ₃ . | SiO ₂ . | Cl. |
|----|-------------------|--------------------|-------|-------|----------------------------------|---------------------------------|-------------------|--------------------|------|
| 1. | 29.02 | 1.12 | 9.43 | 17.90 | 0.46 | 38.40 | 2.87 | 0.38 | 0.54 |
| 2. | 38.94 | 3.84 | 24.08 | 19.88 | 1.22 | 1.54 | 3.53 | 1.31 | 7.30 |
| 3. | 8.04 | 0.94 | 44.00 | 21.52 | 2.77 | 3.28 | 4.46 | 13.85 | 1.47 |
| 4. | 54.24 | 0.42 | 16.61 | 10.01 | 0.67 | 4.44 | 5.50 | 1.43 | 8.62 |
| 5. | 55.66 | 1.65 | 20.08 | 9.47 | 0.91 | 3.73 | 2.94 | 2.00 | 4.59 |
| 6. | 25.50 | 0.81 | 6.58 | 14.70 | 0.42 | 50.84 | 0.97 | 0.15 | 0.03 |
| 7. | 47.36 | 0.99 | 20.91 | 15.88 | 1.09 | 6.83 | 4.98 | 0.80 | 1.50 |

The results show that sunflower is an exhausting crop, especially as regards nitrogen, potash, and phosphoric acid. The oil, which is present in the seeds in large amounts, is one of the most valuable constituents of the plant. The residual cake is at least equal in value to flax seed and cotton seed cakes. N. H. J. M.

Chemical Study of Seed Mangolds. By MARCEL GERBIDON (*Ann. Agron.*, 1901, 27, 135—144).—Mangolds were sown in the spring, and the crop taken up in September of the following year. The composition of (1) the roots, (2) the stalks, and (3) the seed was as follows :

| | Water, per cent. | Per cent. in dry matter. | | | | | |
|----|---------------------|--------------------------|-------|-------------------|------|------|---------------------------------|
| | | Nitrogen. | Ash. | K ₂ O. | CaO. | MgO. | P ₂ O ₅ . |
| 1. | 90.60 | 0.574 | 13.71 | 3.20 | 0.54 | 0.26 | 0.31 |
| 2. | 10.33 | 0.526 | 9.58 | 2.30 | 0.70 | 0.09 | 0.24 |
| 3. | 9.00 | 1.738 | 7.54 | 1.79 | 0.71 | 0.79 | 1.15 |

The yields per hectare of roots, stems, and seeds were 8142, 1850, and 1500 kilos. As a rule, the roots are useless for feeding, but in some seasons they remain succulent, and are suitable for feeding cows. The roots which have produced seed are inferior, especially as regards saccharine and amylaceous constituents, to feeding roots, but the difference is less than might be expected. Seed roots which have failed to produce seed are superior to ordinary feeding roots, having had a longer period in which to accumulate nutritive reserves. Roots which in September, 1899, contained 0.574 per cent. of nitrogen in the dry matter were found to contain 1.232 per cent. in 1900 ; the yield of seed, which should have been about 1500 kilos. per hectare, fell to about 500 kilos. This is attributed to the very dry season ; the roots had accumulated reserve matters, but when the time came for migration to the stems and flowers, the movement was checked by dry weather.

N. H. J. M.

Study of Rations fed to Milch Cows in Connecticut. By WIEBUR O. ATWATER and C. S. PHELPS (10th *Ann. Rep. Storrs Agr. Expt. Stat.* for 1897, 17—66).—Forty-five experiments on thirty-two distinct herds are described. The average yields of milk and butter were 13.2—23.4 and 0.7—1.33 lbs. per day respectively.

† Nitrogenous foods (clover, oats, and peas, cotton seed, linseed, and gluten meals) should be more largely employed. Rations should be made more in accordance with the yield of milk than with the live weight, and with a uniform flow of milk the food need not vary much for variations of 100—200 lbs. live weight. With an increase in the yield of milk, the ration should be increased, the proteids being increased both in quantity and relatively.

N. H. J. M.

Feeding Experiments with Molasses and Maize-germ Molasses. By MAX GERLACH (*Bied. Centr.*, 1901, 30, 102—104 ; from *Jahresber. landw. Versuchsstat. Jersitz b. Posen*, 1898—1899, 48).—Two series of experiments with cows are described. The results indicate that maize-germ molasses may advantageously be replaced by a mixture of liquid molasses, wheat husks, and palm kernel cake.

In pig-feeding experiments, it was found that maize-germ molasses produced 0.65 cwt. more meat than crushed rye.

N. H. J. M.

Feeding Experiments in 1898 and 1899, at Lauchstädt, with Bullocks, Pigs, and Lambs. By FRIEDRICH ALBERT (*Bied. Centr.*, 1901, 30, 94—101 ; from *Landw. Jahrb.*, 1899, 28, 943—995).—To obtain, with pigs, an increase of 0.5 kilo. or more per day, a

ration containing 5 kilos. of digestible proteid per 1000 kilos. of live weight and 28 kilos. of digestible non-nitrogenous matter was found to be suitable; a greater amount of proteids, even with 40 kilos. of non-nitrogenous food, does not give better results than the normal ration. The proteids in fattening rations may be given in the form of meat meal when only an increase of live weight is required. Sugar is a very suitable food when the fattening ration contains 40 kilos. of non-nitrogenous matter (including non-proteids), in addition to 5 kilos. of proteid per 1000 kilos. live weight.

As regards the quality of the meat, the effect of feeding was found to be of less importance than the individual character of the pig.

The results of experiments with bullocks showed that Liebig's meat meal is very suitable; cocoa-husks were found to have a value intermediate between meadow hay and wheat husks, and may be given in amounts of 5 kilos. per 1000 kilos. live weight.

As regards the effect of different kinds of fat in fattening lambs, it was found that sunflower cake gave the best results, being favourable both in increasing the live weight and in improving the meat and fat; rape cake and bran gave good results, but peas, and especially earth-nut cake, were less satisfactory in their effect on the nature of the fat produced.

Maize-germ molasses gave very satisfactory results with lambs.

N. H. J. M.

Factors determining the Richness of Milk. By C. D. SMITH (*Exper. Stat. Record*, 1900, 11, 779; from *Proc. Soc. Prom. Agr. Science*, 1898, 152—155).—From the records of a herd of 25 cows during five years, at the Michigan station, and of 8 cows at the New York State station, the following conclusions are drawn. The milk of a heifer is of as good quality as that of the matured cow. During the first month of lactation the milk is as rich as at any subsequent period, except, perhaps the last few weeks. Season has little effect on the quality of the milk; when cows are at pasture the milk is, on the average, neither richer nor poorer than during winter feeding.

N. H. J. M.

Composition of Sow's Milk. By FRITZ W. WOLL (*Exper. Stat. Record*, 1900, 12, 84; from *Wisconsin Stat. Rep.*, 1899, 267—270. Compare Abstr., 1898, ii, 299).—Analyses of five samples of sow's milk were made. The average composition of sow's milk, according to these and the previous seven analyses, is as follows:—Water, 81.49; fat, 6.60; casein and albumin, 5.75; milk sugar, 5.19; solids not fat, 11.91; ash, 0.97 per cent.

The results of 74 analyses, by the author and others, gives 6.61 as the average percentage amount of fat in sow's milk; this is about 3 per cent. higher than the amount in the milk of cows in the United States.

N. H. J. M.

Soluble Salts of Cultivated Soils. By F. H. KING and J. A. JEFFREY (16th Ann. Rep. *Wisconsin Agr. Expt. Stat.* for 1898—1899, 219—243).—Results of determinations of the soluble salts in soils, at different dates, showed a considerable increase from May to September,

In the first 12 inches of soil, the amount of soluble salts increased from 211·9 to 447·5 lbs. per acre, whilst in the second, third, and fourth 12 inches the amounts increased from 240·2, 164·7, and 59·6 to 347·1, 200·1, and 78·8 lbs. respectively. In the case of plots under growing crops there was a slight tendency for the amount of soluble salts in the upper four feet of soil to decrease rather than increase; but there was no regular decrease in proportion to the amount of dry matter in the produce. Nitric acid was determined in May and in August in the upper four feet of the soil of five plots; two were worked once a week to depths of two and three inches; two once in two weeks to the same depths, whilst the fifth was left. The total gain in nitric acid was from 307 to 378 lbs. per acre, the differences due to different treatment being small; but possibly the results are obscured by variations in the amounts of evaporation.

To ascertain the effect of irrigation on the amount of nitric acid in the soil, determinations were made in the first three feet of soil, which had been irrigated some months previously, and on soil which was not irrigated. Although the irrigated soil had produced the greater crop of maize, it still showed a higher percentage of nitric acid.

N. H. J. M.

Chemical Study of the Phosphoric Acid and Potash Contents of the Wheat Soils of Broadbalk Field, Rothamsted. By BERNARD DYER (*Proc. Roy. Soc.*, 1901, 68, 11—14. Compare *Trans.*, 1894, 65, 115).—Determinations of phosphoric acid and potash (soluble in hydrochloric acid and in 1 per cent. citric acid) were made in 51 samples of Broadbalk soil, including samples taken at three depths of 9 inches, from 12 plots, after the fiftieth crop of wheat had been cut, as well as some earlier samples of surface and subsoil taken in 1881 and in 1865 respectively.

As regards total phosphoric acid, the amounts found in the unmanured and the variously manured soils correspond fairly well with their history; in absence of a known history, the results would not furnish very clear indications. In the case of the subsoils, the irregularities in the soil itself are so great that the total percentage tells nothing.

In the case of phosphoric acid soluble in citric acid, the results obtained both with surface- and frequently with sub-soils are very striking, showing marked accordance with the known history of the plots. In the surface-soils, the average ratio of total phosphoric acid in the soil of the plots manured with superphosphate (with ammonium salts, and both with and without other minerals) to that in the plots which had no phosphoric acid was 1·65 : 1, whilst the ratio of the phosphoric acid soluble in citric acid was 5·46 : 1 for the same groups. The ratios of total phosphoric acid in the two dunged plots to that of the plots receiving no phosphate were 1·78 and 1·36 : 1; the corresponding ratios for soluble phosphoric acid were 6·83 and 3·91 : 1.

The results seem to indicate that for cereals the limit denoting deficiency in phosphoric acid is between 0·01 and 0·03 per cent. soluble in citric acid. In root crops, especially turnips, the limit would probably be higher. By far the greater proportion of phosphoric acid

applied as manure and originally soluble in water is accumulated in the first 9 inches of soil; in the dunged plots, a good deal was found in the second and third 9 inches, and where potassium, sodium, and magnesium salts had been applied without nitrogen, there was evidence of a tangible descent into the second and even third 9 inches of soil. These salts have a distinct influence in retaining phosphoric acid in a less fixed and presumably more available condition. The excess of phosphoric acid applied to the dunged plots is less satisfactorily accounted for; a greater amount has probably passed down to the subsoil than is the case with the chemically manured plots, and some may have become fixed in unavailable forms.

The results of determinations of potassium soluble in strong hydrochloric acid are of interest, but such determinations would, in absence of a known soil history, be of little value except in extreme cases. The citric acid results are, however, very consistent. The ratio of soluble potassium in the surface soil of three plots manured with potassium salts to the average amount of seven plots which had no potassium was 6.75:1; the dunged plots as compared with the same seven plots gave the ratios 10.67 and 9.17:1.

Soil containing 0.01 per cent. of potassium soluble in 1 per cent. citric acid probably requires no further application.

Most of the excess of potassium, applied as manure, is in the first 9 inches of the soil, but a good deal was found (soluble in citric acid) in the second and third 9 inches, especially in the dunged plots and the plot which received superphosphate and sodium and magnesium salts (but no nitrogen) in addition to potassium. Sodium and magnesium salts help to maintain potassium in a form soluble in citric acid. Potassium, although retained by clayey soil to a greater extent than sodium, is far more migratory than phosphoric acid; probably a certain amount is deposited in forms insoluble in dilute citric acid.

N. H. J. M.

Effectiveness of Potassium Nitrate as compared with like amounts of Nitrogen and Potassium in the Form of Potassium Chloride and Sodium Nitrate. By HOMER J. WHEELER and J. A. TILLINGHAST (*Exper. Stat. Record*, 1900, 11, 914—915; from *Rhode Island Stat. Rep.*, 1898, 133—136).—Concordant results were obtained in experiments with grass and mangel-wurzels, indicating that the total yield is greater when sodium nitrate and potassium chloride are applied together than when the same amounts of nitrogen and potassium are given in the form of potassium nitrate. Some special value must therefore be ascribed to sodium or chlorine, or perhaps to both.

N. H. J. M.

Manurial Experiments with Ammonium Sulphate and Sodium Nitrate. By KRAUS (*Bied. Centr.*, 1901, 30, 84—87; from *Vierteljahresschr. Bay. Landw.-rat.*, 1900, 5, 1).—Experiments with barley in 1898 and in 1899 in which sodium nitrate and ammonium sulphate were applied at the same date, showed that both manures gave practically the same results. In 1899, sodium nitrate was applied to a third plot in two lots (two and four weeks later than the application

of nitrate and ammonium sulphate to the other plots); the yield of grain and straw was somewhat increased. N. H. J. M.

Investigations Relative to the Use of Nitrogenous Materials [as Manures]. By E. B. VOORHEES (*Exper. Stat. Record*, 1900, 12, 322—323; from *New Jersey Stat. Rep.*, 1899, 97—120).—Cow dung and a mixture of cow dung and urine were exposed to fermentation and leaching in the open air, in lots of 100 lbs., for about 4 months. The weights were reduced to 50 and 61 lbs. respectively. The dung alone lost nitrogen (46), potash (80), and phosphoric acid (72 per cent.), whilst the mixed excrement lost 57, 72, and 62 per cent. respectively.

Manurial experiments were made on the availability of fresh and leached dung and mixed excrement, both alone and with sodium nitrate, ammonium sulphate, and dried blood. The plants selected were maize and tomatoes, which were grown in a medium clay and in sandy loam respectively, in large, bottomless cylinders. The largest applications of manure were 20 tons per acre.

The results with maize showed, in every case, a distinct gain of dry matter, due to nitrogenous manure, and a considerable, but variable, gain of nitrogen. The total recovery of nitrogen was always greater with mixed materials than when the materials were used singly. The results with dung and sodium nitrate seem to indicate that nitrogen was not lost by denitrification, but that the losses were due to other causes.

The relative availability of the nitrogen, based on the recovery of nitrogen in the crop, was found to be as follows: sodium nitrate, 100; ammonium sulphate, 99.5; dried blood, 95.4; fresh cow dung, 16.76; leached cow dung, 37.86; fresh mixed excrement, 49.66; leached mixed excrement, 50.38. N. H. J. M.

Guano from Erythræa. By G. AMPOLA (*Chem. Centr.*, 1901, i, 757; from *Staz. sperim. agrar. ital.*, 34, 53—59).—The guano contains

| Mois- ture. | Organic substance. | P ₂ O ₅ . | SO ₃ . | CO ₂ . | Cl. | CaO. | MgO. | K ₂ O. | Na ₂ O. |
|----------------|-----------------------|---------------------------------|-------------------|-------------------|------|-------|------|-------------------|--------------------|
| 6.84 | 28.45 | 5.38 | 2.54 | 19.59 | 1.41 | 31.54 | 1.2 | 1.48 | 1.57 |

with traces of ferric oxide, alumina, and silica. The organic substance contains 0.0514 per cent. of ammoniacal nitrogen, and 1.311 per cent. of uric acid; there is no citrate-soluble phosphoric acid. M. J. S.

Box Experiments with Phosphoric Acid from Different Sources. By L. H. MERRILL (*Exper. Stat. Record*, 1900, 11, 913—914; from *Maine Stat. Rep.*, 1898, 64—74).—The experiments included plants of the following orders: *Leguminosæ* (4), *Cruciferae* (4), *Gramineæ* (4), *Solanaceæ* (2), *Umbelliferae* (2), *Polygonaceæ* (1), and *Compositæ* (1 plant).

It was found that plants differed in their ability to feed on crude phosphates. Turnips, cauliflowers, and kohlrabi gave almost as good results with Florida rock as with acid rock, whilst in every other case the good effect of the acid rock was very marked. Barley, maize, and oats seem to require an acid phosphate.

The amount of phosphoric acid soluble in ammonium citrate is not always a measure of its value to the plant. N. H. J. M.

Locusts as Manure. By J. HUNCKEL D'HERCULAIS (*Exper. Stat. Record*, 1900, 11, 913; from *Min. Agr. Argentine Republic*, 1899, pp. 12).—The composition of locusts, according to the analyses of Müntz and Girard, is as follows. In fresh substance, $N=3.15$; $K_2O=0.28$; $P_2O_5=0.60$ per cent. The dry matter contains $N, 11.50$; $K_2O, 1.02$; $P_2O_5, 2.18$, and the dry matter freed from fat, $N, 14.00$; $K_2O, 1.60$, and $P_2O_5, 2.50$ per cent.

When employed alone (400 to 600 kilos. per hectare), locusts were not very effective, but much better results were obtained with a mixture of locusts and superphosphate. Extracting the fat would increase the manurial effect, and would render the decomposition of the locusts inoffensive. N. H. J. M.

Analytical Chemistry.

Improvement in Orsat's Apparatus. By A. BEMENT (*J. Amer. Chem. Soc.*, 1901, 23, 57—58).—A glass disc with a corrugated edge, is interposed between the outlet of the Orsat pipette and the tubes inclosed in the front limb, so that one of the tubes may not drop into the outlet.
L. DE K.

Test for Chlorine for Use with the Blowpipe. By HENRY W. NICHOLS (*Amer. Chem. J.*, 1901, 25, 315—317).—The substance to be tested is powdered, mixed with some previously ignited potassium hydrogen sulphate, and then fused in a tube. Filter paper is moistened with cobalt nitrate solution, and held at the mouth of the tube; if chlorides were originally present, the paper turns a bright blue under the combined action of hydrogen chloride and sulphuric anhydride. Bromides and iodides give a green colour; if both chloride and bromide are present, the colour is first blue and then green. In some cases, especially if much water is given off, it is necessary to dry the paper before the change in colour becomes visible.
J. J. S.

Estimation of Hydrochloric Acid in Gastric Juice. By LÉON MEUNIER (*Compt. rend. Soc. Biol.*, 1901, 53, 283—284).—Colorimetric methods are employed. Toppfer's reaction with dimethyl-aminoazobenzene is rapid and correct. Günzburg's reaction with phloroglucinol-vanillin gives constant results, but is not so quick.
W. D. H.

Method for preparing Normal, Seminormal, Decinormal, &c., Sulphuric Acid of Exact Strength. By RICHARD K. MEADE (*J. Amer. Chem. Soc.*, 1901, 23, 12—15).—A normal sulphuric acid is best prepared by dissolving 124.87 grams of pure crystallised

copper sulphate in 800 c.c. of water, and submitting this solution to electrolysis as directed by Hart and Crossdale (*Abstr.*, 1891, 959), using a current of 2.5 amperes. The copper is generally completely precipitated after 12 hours, and the liquid is then made up to exactly 1 litre.

To prepare a decinormal solution, 12.487 grams of crystallised copper sulphate are dissolved in 750 c.c. of water, and submitted to the action of a current of 1.5 amperes for about 8 hours. The liquid is decanted, the copper well washed, and the whole diluted to 1 litre. (Compare also Kohn, this vol., ii, 190.)

L. DE K.

Estimation of Organic Nitrogen by the Processes of Kjeldahl and Will and Varrentrap. By ALPH VAN ENGELN (*Rev. Intern. Falsific*, 1901, 14, 14—18).—Kjeldahl's process and its various modifications are reviewed. Experiments with leaves of pear-trees and cotton seed meal showed that the highest percentage of nitrogen is obtained by closely following Kjeldahl's original directions, namely, heating for 2 or 3 hours with sulphuric acid, and adding potassium permanganate. For laboratories where nitrogen estimations are not of frequent occurrence, it is more convenient to use Will and Varrentrap's combustion process; the author uses an iron combustion tube.

L. DE K.

The Blondlot-Dusart Method in Chemico-legal cases. By Z. HALÁSZ (*Zeit. anorg. Chem.*, 1901, 26, 438—450).—The author has examined, by the Blondlot-Dusart method, the organs, and especially the brains, of animals which have been poisoned by phosphorus, and those not so poisoned. Tables are given containing the results of the experiments. These show the untrustworthiness of the method. In the case of dogs poisoned by phosphorus, no indication of phosphorus or phosphine was obtained from the brain, but in the stomach, intestines, liver, lungs and kidneys, a smaller or larger indication of phosphorus was always obtained.

E. C. R.

Estimation of Phosphorus in Steel and Iron. By FRED IBBOTSON and HARRY BREARLEY (*Chem. News*, 1901, 83, 122).—When using the lead molybdate method for estimating phosphorus in iron and steel (*Abstr.*, 1900, ii, 757), the graphite may be removed either before or after oxidising with permanganate; in the final stage, after dissolving the yellow precipitate in ammonia, and washing the filter, the solution may be treated with 50 c.c. of a solution containing 8 grams of lead acetate and 400 c.c. of acetic acid (B.P.) in a litre, and the white precipitate ignited and weighed; it contains 0.644 per cent. of phosphorus. For success, many precautions are necessary, and are duly set forth.

Arsenic, if present, is not precipitated with the phosphorus when the precipitation is rapidly effected.

Steels containing 2 to 3 per cent. of chromium frequently dissolve imperfectly in nitric acid of sp. gr. 1.20, even when digested with permanganate, but the addition of an equal bulk of hot water restarts the activity; or hydrofluoric acid may be used for the same purpose,

or 5 c.c. of dilute sulphuric acid (1 : 3), when a further 2 or 3 c.c. of ammonia must be added before precipitating the phosphoric acid.

D. A. L.

Kilgore's Modification of the Volumetric Method of Estimating Phosphoric Acid. By C. B. WILLIAMS (*J. Amer. Chem. Soc.*, 1901, 23, 8—12).—Kilgore's process, titration of the yellow molybdate precipitate with standard solutions of potassium hydroxide and nitric acid (Abstr., 1896, ii, 335), is strongly recommended.

The author prefers diluting the alkali and the acid to such a strength that 1 c.c. shall correspond with 0.0005 gram of phosphoric anhydride.

L. DE K.

Estimation of Phosphoric Acid in Wines by the Official Method. By A. SARTORI (*Chem. Zeit.*, 1901, 25, 263—264).—A criticism of the German official method for estimating phosphoric acid in the ash of wines by the molybdic acid method.

It is stated that the results will be too low unless the temperature at the time of precipitation is raised to 100°; the liquid should also be concentrated to a small volume. The strength of the ammonia when finally precipitating the phosphoric acid with magnesia mixture is not stated in the official instructions, although it is not without influence on the solubility of the precipitate.

L. DE K.

Estimation of Phosphoric Acid in Wines by the Official Method. By RUDOLF WÖY (*Chem. Zeit.*, 1901, 25, 291).—A reply to Sartori (see preceding abstract). The reason that a portion of the phosphoric acid is not precipitated by the molybdate reagent at 80° but only slowly at a higher temperature is explained by the presence of pyrophosphoric acid. In the official process, the ash obtained by evaporating the wine with sodium carbonate and nitre and igniting the residue still contains carbon, which cannot be completely freed from phosphates even by boiling with nitric acid, but requires reburning, which favours the formation of pyrophosphates.

L. DE K.

Estimation of Phosphates in Potable Waters. By A. G. WOODMAN and L. L. CAYVAN (*J. Amer. Chem. Soc.*, 1901, 23, 96—107).—The colorimetric process for the estimation of phosphoric acid in water is criticised at length. As the result of many experiments, the following method is recommended. Fifty c.c. of the sample are mixed with 3 c.c. of nitric acid of sp. gr. 1.07 and evaporated to dryness on the water-bath; the residue is dried in a water oven for 2 hours to render any silica insoluble. The mass is then dissolved in 50 c.c. of water and, without filtering, introduced into the comparison tube. The tubes which have been found to answer best have a capacity of 100 c.c. and are made of hard white glass, about 2.5 cm. in diameter and 24 cm. long to the 100 c.c. mark. Four c.c. of solution of ammonium molybdate (50 grams in 1 litre) and 2 c.c. of nitric acid of sp. gr. 1.07 are added and after 3 minutes the colour is compared with standards made by diluting varying quantities of standard solution of sodium phosphate (1 c.c. = 0.0001 gram P_2O_5) to 50 c.c. and adding the reagents as before. The test analyses are very satisfactory.

L. DE K.

Detection of Arsenic in Beers, Brewing Materials, and Food. By WILLIAM THOMSON and JAMES PORTER SHENTON (*J. Soc. Chem. Ind.*, 1901, 20, 204—208).—Both sulphuric and hydrochloric acids can be freed from arsenic by distillation after adding chromic acid to convert arsenious into arsenic acid. The hydrochloric acid will then be contaminated with chlorine, which must be removed by adding phenol. In Marsh's apparatus, rubber stoppers should be avoided, as they are liable to introduce both antimony and arsenic. Small generating flasks (50 c.c.) one-third filled with zinc are recommended. Granulated zinc is preferred, but the authors have obtained anomalous and unexplained results with various specimens of rod and granulated zinc. The addition of platinic chloride to promote the evolution of hydrogen is deprecated, but it is stated that copper sulphate may be added without seriously diminishing the amount of arsine evolved. The method is made quantitative by preparing comparison mirrors. Beer (50 c.c.) or malt (5 grams) is prepared for testing by destroying the organic matter with sulphuric and nitric acids and then further concentrating to expel the latter. The solution is then diluted and added gradually to the Marsh apparatus from a small stopcock burette.

The authors speak with commendation of the Gutzeit test, and are of opinion that Tyrer's mode of conducting it is an improvement on the original form. In this modification, the gas is freed from hydrogen sulphide by being passed through potash bulbs containing a strong solution of lead acetate, instead of over dry lead acetate paper.

M. J. S.

Estimation of Arsenic and Antimony in Cupreous Materials. By ALLAN GIBB (*J. Soc. Chem. Ind.*, 1901, 20, 184—188).—The substance is dissolved in aqua regia; a small quantity of ferric chloride is added, and then, while heating, sodium carbonate until a small permanent precipitate forms, which contains all the arsenic and antimony as basic ferric salts; this is collected on a filter and washed with hot water until free from nitrates. It is then placed in a fractionating flask with 50 c.c. of a mixture of zinc chloride, cupric chloride, and hydrochloric acid of such concentration as to boil at 108°. About 0.25 gram of pure copper is added, the function of which is to reduce the antimonious and arsenious acids. The neck of the flask is closed by a rubber stopper carrying a thermometer and a stopcock separating bulb, and its side tube is bent and connected with a U-tube containing water and cooled. The mixture is distilled until the boiling point rises to 115°. At that temperature, the whole of the arsenic but none of the antimony will have distilled over. A fresh U-tube is adjusted and the temperature is raised to 150—160°. About 10 c.c. of hydrochloric acid is then cautiously run in. Its vapour sweeps all the antimonious chloride into the U-tube. To this tube tartaric acid is added, the two distillates are nearly neutralised, mixed with sodium hydrogen carbonate, and titrated with *N*/150 iodine.

If the substance to be analysed is readily dissolved by boiling with the cupric zinc chloride solution, it may be introduced into the distillation flask without the preliminary treatment. It is claimed that the

method is more rapid than any other, and if various minor details are attended to is of great accuracy. M. J. S.

Soluble Arsenious Oxide in Paris Green. By SAMUEL AVERY and H. T. BEANS (*J. Amer. Chem. Soc.*, 1901, **23**, 111—117).—A criticism of the methods employed by Haywood (*Abstr.*, 1900, ii, 758) and Hilgard (*ibid.*, 578). In estimating soluble arsenious oxide in Paris green, it must be remembered that the arsenical copper compound is somewhat easily hydrolysed and also that it is partly decomposed by carbon dioxide, particularly if the sample is finely divided.

The following process for the estimation of the soluble arsenious oxide is proposed. One gram of the sample is digested over an open flame with 25 c.c. of a solution of sodium acetate containing 12.5 grams of the crystallised salt. When cold, the solution is made up to 100 c.c. and 50 c.c. are filtered and titrated with standard solution of iodine in the usual way. The presence of sodium acetate largely prevents the hydrolysing action of the water, but no great accuracy is claimed for the process. L. DE K.

Testing Food Products for Boric Acid with Turmeric Paper. By EDWARD H. JENKINS and A. W. OGDEN (*Exper. Stat. Record*, 1900, **12**, 213—214; from *Connecticut State Stat. Rep.*, 1899, 153—155).—Free boric acid cannot be readily detected with turmeric paper in presence of borates. Hydrochloric acid must be added in considerable excess. When less than 1 part of boric acid is present in 10,000 parts of solution, certain results are not to be expected. N. H. J. M.

Sodium Ferrisalicylate; Estimation of Boric Acid in Borates of the Alkalis and Alkaline Earths. By JULES WOLFF (*Zeit. Nahr. Genussm.*, 1901, **4**, 157—160. Compare *Abstr.*, 1900, ii, 435).—The indicator is best prepared by saturating a concentrated solution of normal sodium salicylate with freshly precipitated well-washed ferric hydroxide at 80°. According to Gerock, the reagent contains a sodium salt of ferrisalicylic acid (*Abstr.*, 1900, ii, 769). Alkaline borates are titrated as follows. The sample is dissolved in 25 c.c. of water and mixed with 1 or 2 c.c. of the indicator and dilute hydrochloric acid is added until the colour turns violet; aqueous sodium hydroxide is then added until the colour turns pale orange. Twenty c.c. of glycerol are now added and a few drops of solution of phenolphthalein and the boric acid is then titrated with *N* sodium hydroxide. Calcium borate (boracite) is dissolved in slight excess of hydrochloric acid, the solution diluted with water and any carbon dioxide expelled by boiling in a reflux apparatus; the liquid is then treated as described above.

If the sample should contain aluminium compounds, these may be removed by means of ammonia. The ammonia is then in turn expelled by boiling with excess of aqueous sodium hydroxide. L. DE K.

Detection of Acid Carbonates in Waters. By M. E. POZZI-ESCOT (*Ann. Chim. anal. appl.*, 1901, **6**, 135—136).—The author revives the proposal made by Jaquemin in 1888 to use his ferroso-

pyrogallol reagent for the detection of acid carbonates in water. Half a gram of pyrogallol is dissolved in 5—6 c.c. of distilled water and 2 drops of the official solution of ferric chloride are added. A few drops of this brown reagent are added to 200—250 c.c. of the water to be tested. The smallest traces of acid carbonates produce an amethyst-violet coloration, which deepens gradually to a violet-black. The absence of ammonia must first be assured.

M. J. S.

Estimation of Calcium by the Citrate Method. By MAX PASSON (*Zeit. angew. Chem.*, 1901, 14, 285—286. Compare Abstr., 1900, ii, 246).—When the amount of calcium is very small, it does not always separate properly on the application of the author's citrate process; the method has therefore been slightly modified.

The hydrochloric acid solution of the soil is mixed with dilute ammonia until a slight permanent precipitate is produced, when 25 c.c. of Wagner's citric acid solution (20 grams of citric and 0.1 gram of salicylic acid per litre) are added without delay. When the precipitate has redissolved, which should occupy only a few minutes, another 12—13 c.c. of Wagner's solution are added, the liquid is diluted to 200 c.c. and heated to boiling. Solid ammonium oxalate is now added little by little until no further precipitate is formed, and when the liquid has become clear it is again tested by adding a solution of ammonium oxalate. After standing overnight, the calcium oxalate is collected and treated as usual.

L. DE K.

Estimation of Calcium and Magnesium in Natural Waters. By LUDWIG W. WINKLER (*Zeit. anal. Chem.*, 1901, 40, 82—92).—Clark's soap test can be so modified as to afford an accurate as well as rapid method for estimating both calcium and magnesium in natural waters. If to a solution which contains both metals there be added a small quantity of potassium sodium tartrate with some potassium hydroxide, the soap solution will estimate the calcium only; but if ammonium chloride and ammonia are added, both the calcium and magnesium will consume soap, magnesium requiring one-third more soap than the equivalent quantity of calcium.

The following solutions are required:—1. *Tartrate solution.* One hundred grams of potassium sodium tartrate and 6 grams of potassium hydroxide are dissolved to 500 c.c.

2. *Ammonia solution.* Ten grams of ammonium chloride and 100 c.c. of 10 per cent. ammonia are made up to 500 c.c.

3. *Barium chloride solution.* 4.363 grams of the crystallised salt are dissolved to 1 litre. This solution is of 100° (German) hardness; 10 c.c. of it, diluted to 100 c.c., and mixed with 5 c.c. of solution 1, are used for standardising the soap solution.

4. *Soap solution.* Fifteen grams of pure oleic acid are shaken with 600 c.c. of alcohol (90—95 per cent.), 400 c.c. of water, and 4 grams of potassium hydroxide. The filtered solution is further diluted with alcohol and water until it agrees exactly in strength with solution 3.

To estimate calcium, the water is diluted so far that 100 c.c. will not require more than 10 c.c. of soap solution; that quantity is mixed with 5 c.c. of solution 1, and the hardness estimated in the usual

manner. Since 1.786 grams of calcium carbonate per litre constitutes a solution of 100° (German) hardness, the number of c.c. of soap solution multiplied by 7.143 and corrected for dilution gives the number of mg. of calcium per litre of the original water. To estimate both calcium and magnesium, 100 c.c. of the diluted water are mixed with a further quantity of 100 c.c. of distilled water and 5 c.c. of solution 2. In this titration, it is essential that the lather should persist for at least 5 minutes. The difference between the two titrations, diminished by $\frac{1}{4}$, and multiplied by 4.357 gives mg. of magnesium per litre. Mineral waters containing large amounts of carbon dioxide should be coloured with methyl-orange, neutralised with hydrochloric acid, boiled, cooled, and diluted.

It is noteworthy that the volume of soap solution required is proportional to the hardness, which in Clark's original process is not the case. The presence of free alkali renders the end reaction sharp by preventing the hydrolysis of the potassium oleate. M. J. S.

Solubility of Barium Sulphate in Solutions of Sodium Thiosulphate. By LEONARD DOBBIN (*J. Soc. Chem. Ind.*, 1901, 20, 218—219).—The fact that barium sulphate is markedly soluble in solutions of sodium thiosulphate has been pointed out by Fresenius, and by Salzer (Abstr., 1892, 1514) but appears to be very generally ignored. The addition of dilute nitric acid augments the solubility greatly; hydrochloric acid has a similar, but more feeble action. The author does not fix the limits of solubility, but shows that 0.0142 gram of sodium sulphate in 20 c.c. of *N*/20 thiosulphate mixed with an equal volume of 20 per cent. nitric acid remains perfectly clear with barium chloride. M. J. S.

Estimation of Magnesium by Organic Bases. By W. HERZ and K. DRUCKER (*Zeit. anorg. Chem.*, 1901, 26, 347—349).—The method of estimating zinc by precipitation with an aqueous solution of dimethylamine is applicable to magnesium and gives accurate results (this vol., ii, 240). Magnesium salts are also completely precipitated by a solution of free guanidine; the precipitate of magnesium hydroxide is treated in the usual way. The authors point out that this method is specially advantageous for estimating magnesium in the presence of alkalis, and for the analysis of mixed silicates containing magnesium. E. C. R.

Volumetric Estimation of Mercuric Chloride in Surgical Dressings. By F. UTZ (*Chem. Centr.*, 1901, i, 595; from *Pharm. Centr.*, 1901, 42, 81).—Archetti's method (*Boll. Chim. Farm.*, 39, 765) gives very satisfactory results. Twenty grams of the dressing are digested at 70—80° for several hours with 200 c.c. of a 0.5 per cent. solution of sodium chloride, and the extract is titrated with *N*/10 ammonia and phenolphthalein. The red colour is not obtained until all the mercury is precipitated; 1 c.c. of *N*/10 ammonia = 0.00271 gram of mercuric chloride (compare Abstr., 1900, ii, 762; this vol., ii, 204). M. J. S.

Estimation of Mercury in Official Hydrargyrum Salicylicum. By ERWIN RUPP (*Arch. Pharm.*, 1901, 239, 114—118).—According to the German pharmacopœia (4th ed.), 0.3 gram of this drug should

yield 0.2 gram of mercuric sulphide when it is dissolved in aqueous salt solution, the solution acidified with a little hydrochloric acid, and then precipitated with hydrogen sulphide. This only happens, however, if the precipitation is effected at 100° or thereabouts; a white, gelatinous precipitate is produced first, and in the cold this is not converted into the sulphide. Hydrochloric acid precipitates a substance of the composition $C_7H_5O_3 \cdot HgCl$; in neutral solution, hydrogen sulphide gives a precipitate of the composition $C_7H_5O_3 \cdot Hg \cdot SH$. In both these compounds and in the original salicylate, the mercury is probably attached to the aromatic nucleus (compare Dimroth, *Abstr.*, 1889, i, 54, 528).

The salicylate may also be analysed by pounding it with a little water, allowing it to remain for an hour with 25 c.c. of *N*/10 iodine solution, and titrating the excess of the latter with thiosulphate. Of the commercial product, 0.3 gram requires 16.5–16.8 c.c. of *N*/10 iodine; a sample purified by dissolving it in dilute aqueous sodium hydroxide filtering, and precipitating with acetic acid, required nearly the theoretical amount, 17.85 c.c.

C. F. B.

Detection of Lead in Drinking Waters. By A. BELLOCQ (*J. Pharm.*, 1901, [vi], 13, 56–57).—Water containing even the merest trace of lead presents to the trained eye a decided haze, which disappears on adding nitric acid; the author concludes that the metal exists in combination with an organic substance.

To detect the metal, one or two litres of the suspected water are mixed with 5–10 c.c. of an ammoniacal solution of zinc, and when the supernatant liquid has become perfectly clear, it is carefully decanted and the deposit collected on a small filter. It is then dissolved in warm acetic acid containing a little ammonium acetate, and any lead present is tested for with potassium chromate.

L. DE K.

Estimation of Aluminium in Steel. By E. SPATZ (*Zeit. öffentl. Chem.*, 1901, 7, 60–62).—About 1 gram of aluminium-steel is dissolved in a platinum dish in a mixture of 20 c.c. of water and 2 c.c. of sulphuric acid; during the heating on the water-bath, the dish is covered with another platinum dish. When the steel is dissolved, the liquid is rinsed into a platinum or silver dish holding 400 c.c.; 40 grams of ammonium oxalate are added, and the liquid is submitted to electrolysis until only traces of iron are left in solution. The liquid is then siphoned off and evaporated to dryness in a platinum dish; the residue is ignited, and fused with a known weight of potassium hydrogen sulphate. The fused mass is dissolved in water and a few drops of sulphuric acid mixed with a few drops of a solution of ammonium phosphate, and then with excess of dilute ammonia; the precipitate is purified by dissolving it off the filter in warm dilute hydrochloric acid and reprecipitating with ammonia, when it is washed, dried, ignited, and weighed as aluminium phosphate + ferric phosphate. The precipitate is again fused with a known weight of potassium hydrogen sulphate; the fused mass is dissolved in dilute sulphuric acid, and the iron reduced to the ferrous state by means of a known weight of zinc; it is then titrated with permanganate. A blank experiment is made, using exactly the same

quantities of the various reagents, and any aluminium found is allowed for.

L. DE K.

Chemical Analysis of Soils. By B. SJOLLEMA (*Chem. Zeit.*, 1901, 25, 311—312).—A criticism of Dyer's method (*Trans.*, 1894, 65, 115). The phosphates soluble in a 1 per cent. solution of citric acid are not properly extracted unless the sample is treated repeatedly with fresh quantities of the solvent.

L. DE K.

Analysis of Soils. By J. ALAN MURRAY (*Analyst*, 1901, 26, 92—96).—A criticism of the method proposed by Hall and others (this vol., ii, 80). The author thinks that the constituents should be reported in ounces per cubic foot, which is practically the same as grams per cubic decimetre. The scheme should also include a determination of organic carbon, from which the amount of humus may then be calculated, as this contains an average of 50 per cent. of carbon. In one case, it was found that a considerably larger proportion of a available phosphoric acid was obtained by extracting the undried sample. It is also pointed out that the stones contained in the soil should also be tested to ascertain whether they yield any available plant food.

L. DE K.

The Detection and Estimation of Minute Quantities of Manganese. By HUGH MARSHALL (*Chem. News*, 1901, 83, 76).—Oxidation by means of a persulphate is accelerated by the addition of silver nitrate. Minute quantities of manganese may be detected by gently warming the solution with potassium or ammonium persulphate, a moderate quantity of sulphuric or nitric acid, and a drop of silver nitrate solution; a distinct permanganate coloration is obtained in half a c.c. of solution containing 0.001 mg. of manganese. By taking known quantities and comparing with standard permanganate solutions, the method may be used quantitatively.

D. A. L.

Estimation of Iron in Human Urine. By PAUL HOFFMANN (*Zeit. anal. Chem.*, 1901, 40, 73—82).—See this vol., ii, 326.

Separation of Ferric Chloride in Aqueous Hydrochloric Acid from other Metallic Chlorides by Ether. By FRANK L. SPELLER (*Chem. News*, 1901, 83, 124—125).—Ether removes ferric chloride from its solution in hydrochloric acid whilst other chlorides are mostly insoluble, and Rothe based a method for the separation of iron on this property. The author now shows that the separation is most effective with hydrochloric acid ranging in sp. gr. from 1.100 to 1.115 used in small quantity. In analytical work, the solution of the mixed chlorides is treated with nitric acid, evaporated to a syrupy condition, dissolved in as small a quantity of hydrochloric acid of sp. gr. 1.105 as possible, and extracted with ether in a separating funnel, using 5 c.c. of ether for every decigram of iron present; a second treatment with ether or a single precipitation with ammonia removes any iron remaining in the aqueous solution.

D. A. L.

The Assay of Gold Sodium Chloride. By JOHNSON and SONS (*J. Soc. Chem. Ind.*, 1901, 20, 210).—Fifteen grains of the substance are dissolved in an ounce of water, the gold is precipitated by sul-

phurous acid, collected on a filter, dried, ignited, and weighed. The error of the assay is ascertained by dissolving 7 grains of pure gold in aqua regia, evaporating, redissolving, and reducing in exactly the same manner, and the corresponding correction is made in the result.
M. J. S.

Estimation of Organic Carbon in Water. By JOSEF KÖNIG (*Zeit. Nahr. Genussm.*, 1901, 4, 193—201).—Five hundred c.c. of the sample are filtered through asbestos contained in a Gooch crucible. The filtrate is mixed with 10 c.c. of dilute sulphuric acid and boiled for half an hour to expel carbon dioxide in a round bottomed flask furnished with a dropping funnel to which a soda-lime tube is attached, and with a specially constructed condensing tube. Two or three grams of potassium permanganate, 10 c.c. of a 20 per cent. solution of mercuric sulphate and another 40 c.c. of dilute sulphuric acid are added, and the boiling is continued after connecting the condensing tube with a Peligot tube containing a little sulphuric acid, and a U-tube containing calcium chloride to absorb any moisture; the carbon dioxide resulting from the oxidation of the carbon is then absorbed in two weighed soda-lime tubes connected with a guard tube filled partly with soda-lime and calcium chloride.

The carbon in the suspended matter may also be estimated in this apparatus, using a 250 c.c. boiling flask, by heating the asbestos with 10 c.c. of mercuric sulphate solution, 10 c.c. of a 50 per cent. solution of chromic acid, and 50 c.c. of strong sulphuric acid.

If the sample is suspected of containing volatile carbon compounds, it is at once oxidised with sulphuric acid, mercuric sulphate, and potassium permanganate, allowance being made for the carbon dioxide in the water.
L. DE K.

Source of Error in the Permanganate (Kubel-Tiemann) Process for Estimating Organic Matter in Potable Water. By MAURICE DUYK (*Ann. Chim. anal. appl.*, 1901, 6, 121—126).—The author, who employs that modification of the permanganate process which consists in boiling the water with permanganate and sulphuric acid, calls attention to the large errors caused by the presence of chlorides (compare Abstr., 1886, 581; this vol., ii, 201). The error may be completely obviated by shaking the water for an hour or two with enough moist silver oxide to remove all the chlorine.

M. J. S.

Microchemical Distinction of the Hydrocarbons of Coal Tar. By THEODOR H. BEHRENS (*Rec. Trav. Chim.*, 1900, 19, 386—397).—I. *Solid Hydrocarbons*.—The reagent used is α -dinitrophenanthraquinone. This gives *rhombs* with naphthalene, acenaphthene, indole, anthracene, and carbazole. *Yellow rhombs*, naphthalene, confirmed by the formation of small, red rhombs with chrysamic acid. *Brown rhombs*, indole, confirmed by giving with chloranil chocolate prisms showing a dichroism into black. *Orange rhombs*, acenaphthene, giving with chrysamic acid bluish-green needles, showing a dichroism into blue. *Grey rhombs*, with dichroism into blue, anthracene; confirmed by giving green needles with chrysamic acid and by

yielding on oxidation with chromic acid in glacial acetic acid solution anthraquinone, crystals of which from nitrobenzene show an axial extinction in polarised light. *Violet rhombs*, carbazole, which gives green needles with chrysamic acid and is destroyed by chromic acid.

Brown prisms are formed by α -dinitrophenanthraquinone with fluorene and phenanthrene. The former volatilises with naphthalene in a current of steam, and the product of oxidation by chromic acid is not a quinone; the latter sublimes with anthracene, and yields a yellow ortho-quinone on oxidation, characterised by uniting with *o*-phenylenediamine to form yellow crystals of the phenazine which are coloured red by concentrated hydrochloric acid, and by yielding with carbazole in nitrobenzene solution copper-coloured rhombs of an additive product.

Red needles are formed by α -dinitrophenanthraquinone with chrysene, which sublimes *after* anthracene. *Brownish-red rods* (tiges) are formed with difficulty by pyrene, which gives small rod-like greenish-black crystals with chrysamic acid, sublimes with chrysene, from which it can be separated by alcohol, and yields on oxidation a red para-quinone.

II. *Liquid Hydrocarbons*.—These are nitrated and the nitro-compounds reduced by means of ammonium sulphide to bases which are characterised by the action of a solution of iodine in potassium iodide on their hydrochlorides in presence of sulphuric acid (acid solution) or of potassium sulphate (neutral solution).

A. The neutral or acid solutions give red or brown sulphates; aniline (dichroic), *o*-, *m*-, and *p*-toluidine (non-dichroic).

B. Neutral solutions give reddish sulphates; acid solutions, grey, dichroic hydriodides; *v-o*-xylidine, *p*-xylidine, *s-ψ*-cumidine.

C. Neutral and acid solutions yield only a grey hydriodide: α -*m*-xylidine.

Illustrations are given of the forms of the principal crystalline derivatives referred to of the solid constituents of coal tar.

W. A. D.

Comparative Method for Determining the Fusing Points of Asphalts. By CHARLES F. MABERY and OTTO J. SIEPLEIN (*J. Amer. Chem. Soc.*, 1901, 23, 16—20).—In a glycerol-bath is placed a narrow beaker closed by a cork, through which is passed a thermometer and a strip of metal; the lower end of the strip is bent at right angles, the corners are turned up, and the section of asphalt, large enough to project on either side of the metal, is pressed on the points so formed. The temperature is noted at which the specimen becomes sufficiently fluid to fall on either side of the metal support and just touch the bottom of the beaker. In order to obtain comparable results, the distance of the thermometer from the specimen, the distance of the metal from the bottom of the beaker, the width of the metal strip, and the dimensions of the specimen must be kept constant.

E. G.

Rapid Method for the Determination of Prussian Blue in Spent Oxide. By JAS. M. POPPLEWELL (*J. Soc. Chem. Ind.*, 1901, 20, 225).—Five grams of the substance are boiled for 5 minutes with

50 c.c. of a 5 per. cent. solution of sodium hydroxide. The filtered extract and washings are precipitated hot with excess of ferric chloride and hydrochloric acid. The precipitate is collected on a filter, washed, and then treated in the cold with a similar quantity of sodium hydroxide for 10 minutes. The solution so obtained is acidified with sulphuric acid and titrated with a solution of copper sulphate (12.48 grams per litre) until a drop on filter paper gives no blue colour with a contiguous spot of ferric chloride. M. J. S.

Detection of Methyl Alcohol in Vinegar. By R. ROBINE (*Ann. Chim. anal. appl.*, 1901, 6, 127—129).—Although it is commonly believed that *Mycoderma aceti* cannot develop in methyl alcohol, it is nevertheless possible to employ a certain proportion of methylated spirit in the manufacture of vinegar. Since the methyl alcohol escapes oxidation, its detection in the vinegar by Trillat's process (Abstr., 1889, ii, 130; 1900, ii, 111) serves for the discovery of this fraud. A litre of the vinegar is distilled through a Le Bel fractionating tube. The first 400 c.c. are made alkaline, 100 c.c. are distilled off and oxidised by 5 grams of potassium dichromate and 20 c.c. of sulphuric acid (1:5). After an hour, the liquid is distilled. The first 2—3 c.c. which contain acetaldehyde are rejected, and the following 50 c.c. are heated with pure dimethylamine in a corked flask for $2\frac{1}{2}$ hours. The mixture is then made alkaline and the excess of dimethylamine distilled off. If the contents of the flask are then yellow, or turbid, the acetaldehyde has been imperfectly expelled, and the whole operation must be repeated. If colourless, acetic acid and lead dioxide are added, and the mixture boiled. The production of a pure blue colour (which disappears on cooling) is conclusive as to the presence of methyl alcohol, but a dubious greenish-blue coloration may be obtained if the acetaldehyde has not been completely removed. M. J. S.

Dilution of Wine and its Detection. By ARMAND GAUTIER, ALLYRE CHASSEVANT and LOUIS MAGNIER DE LA SOURCE (*J. Pharm.*, 1901, [vi], 13, 14—18).—As the result of six analyses of wines which were poor but not diluted with water, and also having regard to the fact that the volatile acidity may increase by storage, the authors now propose the following rule for determining whether a sample has probably been watered.

The fixed and the volatile acidity are each taken separately and calculated as sulphuric acid per litre. If the volatile acidity exceeds 1, the unit is added to the fixed acidity; the sum represents the joint acidity before souring. The excess of volatile acidity is divided by 10 and added to the alcoholic titre (percentage of alcohol by volume). In a sample which has not been diluted, the sum of the alcoholic titre and joint acidity per litre should not be less than 12.5. L. DE K.

Wine Analysis. Modification of the "Sum of Alcohol-Acid Rule." By FERDINAND JEAN (*Rev. Intern. Falsif.*, 1901, 14, 18—19).—The author approves of the modification proposed by Gautier, Chassevant, and Magnier de la Source (preceding abstract). L. DE K.

Volumetric Estimation of Phenol. By JAMES F. TOCHER (*Pharm. J.*, 1901, [iv], 12, 360—361).—The estimation of phenol in

aqueous solutions may be effected by the following process. The solution is rendered alkaline with sodium hydrogen carbonate, excess of decinormal potassium permanganate added, the liquid boiled for 5 minutes, allowed to cool, and then acidified with sulphuric acid; the mixture is now warmed to 60° and titrated with decinormal oxalic acid. It is found that 29.78 c.c. of the permanganate solution are required for 0.01 gram of phenol, in accordance with the equation $C_6H_5 \cdot OH + 7O_2 = 6CO_2 + 3H_2O$. E. G.

A Simple Fermentation Saccharimeter. By PAUL HAMBERGER (*Chem. Centr.*, i, 718; from *Pharm. Zeit.*, 46, 174).—A wide-necked bottle of 25 c.c. capacity, is provided with a caoutchouc stopper, through which passes a straight glass tube, 30 cm. in length and 6 mm. diameter, which is graduated from the upper end into 20 portions of 0.29 c.c. each. In the bottle are placed 100 grams of mercury, 10 c.c. of the sugar solution, containing about 0.1 gram of sugar, a sufficient quantity of yeast, and water up to the neck. The stopper is then inserted, with the tube dipping into the mercury, but avoiding the entrance of the aqueous liquid into the tube. By forcing in the stopper, the mercury is driven up the tube until its level can be noted. The bottle is then plunged for 2 hours into water of 34—36°. According to the author's experiments, 0.1 gram of sugar will in that time furnish a quantity of carbon dioxide, which, together with the expansion of the liquids, will raise the level of the mercury in the tube through 10 divisions. M. J. S.

A New Sugar Reaction. By OFFER (*Chem. Centr.*, 1901, i, 646; from *Med. Woch.*, 1901, 81).—Five c.c. of urine are heated to boiling with a small quantity of phenylhydrazinesulphonic acid and then mixed with 10 c.c. of 15 per cent. sodium hydroxide solution. After cooling and shaking, a rose-red coloration is produced if more than 0.1 per cent. of sugar is present. A similar reaction is obtained with naphthylhydrazinesulphonic acid, also with phenylhydrazine salicylate or acetate. M. J. S.

Estimation of Reducing Sugars in Blood. By G. MEILLÈRE and P. CHAPELLE (*J. Pharm.*, 1901, [vi], 13, 257—262).—A measured quantity of blood (20—30 c.c.) is heated to boiling as soon as possible after being drawn, to arrest the action of ferments. The clots are crushed, and there are added 1 drop of acetic acid, 5 c.c. of a saturated solution of zinc acetate, and 10 grams of sodium sulphate. The mixture is again boiled, and the liquid extracted from the clot either by a centrifugal machine or by a press and subsequent filtration. When completely clarified, it is divided between two tubes, which are plunged into boiling water. In each are dissolved 2.5 grams of a mixture of 10 parts of tartaric acid and 7 parts of copper sulphate, and then 8 c.c. of potassium hydroxide solution (containing 1 gram per c.c.). After 15 minutes, the cuprous oxide is separated, washed by centrifuging, and weighed after drying at 120°. It should be calculated into dextrose, the factor being ascertained by comparative experiments made under identical conditions, but inasmuch as several carbohydrates

may be present, much information may be gained from estimations made before and after hydrolysis, and after fermentation with yeast.

M. J. S.

Estimation of Sugar in Urine by Lehmann's Method. By O. GOETZEL-ALBERS (*Chem. Centr.*, 1901, i, 706; from *Pharm. Zeit.*, 46, 156).—In processes of sugar estimation by Fehling's solution which depend on the amount of unreduced copper being ascertained, it is sometimes necessary, after reduction, to clarify the solution by filtration through paper. Since paper retains copper, it is, in that case, essential that the standard should consist of Fehling's solution, appropriately diluted, filtered through a paper of the same size.

M. J. S.

Estimation of Sugar in certain Urines. By GUSTAVE PATEIN (*J. Pharm.*, 1901, [vi], 13, 176—177).—The author has met with a urine containing methylene-blue in sufficient quantity to communicate a green colour to the sample. On adding basic lead acetate, the yellow colouring matter of the urine was precipitated, leaving a filtrate of a decided bluish colour unfit to be examined for sugar in the usual way. The colouring matter was, however, completely removed on adding mercuric nitrate.

L. DE K.

Estimation of Sugar in Vinous Products. By A. BERNARD (*Ann. Chim. anal. appl.*, 1901, 6, 89—95).—Ten c.c. of grape juice, or similar liquid suitably diluted, are mixed in a conical flask with 20 c.c. of Fehling's solution and rapidly heated to boiling. In order to prevent any sensible loss by evaporation, the flask is then at once cooled by placing it in water. When cold, the liquid is filtered and 15 c.c. (or more) of the filtrate are titrated with solution of potassium cyanide until colourless. The cyanide solution is conveniently made of such a strength that 10 c.c. are just sufficient to decolorise 10 c.c. of Fehling's solution. The exact strength of the latter may be ascertained by means of an accurately made solution of invert sugar.

L. DE K.

Estimation of Sucrose and Lactose in Condensed Milk. By SEVERIN H. R. RIIBER and C. N. RIIBER (*Zeit. anal. Chem.*, 1901, 40, 97—110).—The method worked out by Kjeldahl for the estimation of two sugars simultaneously present in a solution (*Abstr.*, 1896, ii, 580), appears to be based on the postulate that the amount of copper yielded by one of the sugars bears the same proportion to the amount of that sugar present as the total copper obtained would bear to the amount of the same sugar which would be necessary to produce the total reduction observed. This is only absolutely correct when the two sugars reduce Fehling's solution with equal rapidity, but when it is applied to a mixture of invert sugar and lactose, the former of which reduces much more rapidly than the latter, an inaccuracy appears in consequence of the invert sugar acting chiefly on a strong copper solution, and the lactose on a relatively enfeebled one. The error can, however, be avoided by the following device. From a pair of titrations (one before and the other after inversion) an approximate result is calculated. Expressing the percentage of sucrose found as $K.R$, in which

R is the true percentage, the value of K may be ascertained within the limits of experimental error by preparing a solution of pure sucrose and lactose, having the composition indicated by the approximate result, and titrating this in exactly the same manner. The practical method of procedure is as follows. Ten grams of the condensed milk are mixed with 400 c.c. of water in a 500 c.c. flask. The casein and fat are precipitated by adding 10 c.c. of copper sulphate (69.278 grams per litre), followed by 10 c.c. of sodium hydroxide (10.2 grams per litre). After making up and filtering, 50 c.c. of the filtrate are titrated by Kjeldahl's process (*loc. cit.*). This gives the approximate percentage of lactose, $K.L$. Fifty c.c. are then inverted by mixing with 10 c.c. of $N/5$ hydrochloric acid, and plunging for exactly 30 minutes into boiling water; the acid is neutralised by 10 c.c. of $N/5$ sodium hydroxide, the liquid cooled and made up to 100 c.c., of which 25 c.c. are titrated in exactly the same manner. Taking from Kjeldahl's table the amount of lactose which would reduce the total amount of copper found in the second titration, the proportional weight of copper resulting from the lactose found in the first titration is calculated. The difference is the copper reduced by the invert sugar, and the amount of invert sugar which has produced it is proportional to the amount (read from the table) which would have yielded the total copper found. Multiplying by 0.95 to convert invert sugar into sucrose, the value of $K.R$ is obtained. A solution is now prepared containing $K.L$ per cent. of lactose, and $K.R$ per cent. of sucrose, and by a precisely similar pair of titrations and a calculation made in the same manner, the value of K is obtained. Since the error in the percentage of lactose is nearly proportional to the amount of sucrose present, it is best to put $L = KL - K'R$. Then from the titrations with known weights of the pure sugars (L' and R'), there is obtained an equation from which the value of K' is found, and thence the true percentage of lactose (L).

If the object is to ascertain the percentage of refined cane sugar in the condensed milk, instead of that of pure sucrose, a similar method of analysis must be employed to find the percentage of sucrose in the refined sugar.

An example will render the method of calculation clearer. A sample of milk gave $K.R = 41.43$ per cent., and $K.L = 14.99$ per cent. A solution made up with 4.15 grams of sucrose and 1.5 grams of lactose in 500 c.c. showed, on analysis, 4.072 grams of sucrose and 1.609 grams of lactose, whence $K = 0.9813$, and $K' = 0.0263$ ($4.15 K' = 1.609 - 1.5$), and the true values for the milk were $R = 42.22$ per cent., and $L = 13.88$ per cent. ($14.99 - 0.0263 \times 42.22$).

The method applied to three samples of milk prepared with known amounts of sucrose gave extremely close results. M. J. S.

The so-called Furfuraldehyde Tests for Carbohydrates. By CARL NEUBERG (*Zeit. Ver. deut. Zuckerind.*, 1901, 270—279).—A number of sugars and sugar-like compounds have been submitted to the following carbohydrate tests: (1) the α -naphthol test of Molisch (*Abstr.*, 1886, 923), and von Udránsky (*Abstr.*, 1888, 878); (2) Seliwanoff's resorcinol test (*Abstr.*, 1887, 459); (3) Tollen's phloroglucinol test (*Abstr.*, 1889, 847; 1896, ii, 504), and (4) the orcinol

test (see Tollens, *Annalen*, 1890, 260, 304). The following table contains a *résumé* of the results obtained, the sign + or - indicating that the compound does or does not answer to the test concerned :

| | Resor- cinol. | | Phloro- glucinol. Orcinol. | |
|-------------------------------------|----------------------------|---|-------------------------------|----------|
| | α -Naphthol. | | | |
| Glycolaldehyde | + | - | - | - |
| Glyceraldehyde..... | + | - | + | (weak) + |
| Glycerose { (a) prepared with NaOBr | + | + | - | + |
| | (b) from lead glycerate... | + | + | (weak) + |
| <i>l</i> -Erythrose | + | - | + | (weak) - |
| <i>i</i> -Tetrose | + | + | + | (weak) - |
| <i>d</i> -Lyxose | + | - | + | + |
| <i>d</i> -Arabinose..... | + | - | + | + |
| <i>r</i> -Arabinose | + | - | + | + |
| <i>l</i> -Keto-arabinose | ? | + | ? | ? |
| <i>i</i> -Keto-galactose | ? | + | - | - |
| <i>d</i> -Oxygluconic acid | + | + | + | + |
| Aldehydomucic acid | + | - | + | + |
| Formose | + | + | + | + |

T. H. P.

Estimation of Carbohydrates in Human Fæces. By JOSEF STRASBURGER (*Pflüger's Archiv*, 1901, 84, 173—190).—The estimation of carbohydrates in fæces is a new field, and the whole of the present paper is occupied with a description of methods, several of which were tested, for the estimation of sugar and starch. The Volhard-Pflüger method for sugar gave the best results, although there was always some loss. Starch, even in small quantity, can also be estimated with certainty. Results are promised in a future paper. W. D. H.

Titration of Salicylic Acid, Salicylates, and Phenol. By FERNAND TELLE (*J. Pharm.*, 1901, [vi], 13, 49—56).—The process is based on the fact that a solution of sodium hypochlorite added to a solution of potassium bromide acidified with hydrochloric acid liberates bromine. If the solution contains salicylic acid or phenol, no bromine will be set free until the former has been converted into the dibromo- and the latter into the tribromo-compound. The hypochlorite is prepared by diluting 35 c.c. of the commercial product to a litre, and its exact bromine liberating power is found by titrating it with potassium bromide and a known weight of arsenious acid.

Salicylic Acid.—One gram of the sample is dissolved in 2 c.c. of aqueous sodium hydroxide of sp. gr. 1.2 and 50 c.c. of water, and diluted to 500 c.c. Twenty-five c.c. (0.05 gram of the sample) are then mixed in an Erlenmeyer flask with 5 c.c. of a 10 per cent. solution of potassium bromide and 10—15 drops of hydrochloric acid, and the hypochlorite is added from a burette until the precipitation is almost complete. Five c.c. of chloroform and a little alcohol are now added to dissolve the precipitate, and the addition of hypochlorite is continued until the chloroform turns yellowish from the presence of free bromine.

Sodium, Lithium, and Magnesium Salicylates.—These are titrated like the free acid ; there is no need for dissolving in aqueous sodium hydr-

oxide. *Bismuth salicylate*. One gram is boiled with 25—30 c.c. of water and 3 c.c. of aqueous sodium hydroxide for 10 minutes. When cold, the liquid is diluted to 250 c.c. and 25 c.c. are taken for the titration. *Phenol*. One gram is dissolved in a litre of water and 25 c.c. are titrated as before; it is not necessary to use chloroform, the end reaction being shown by the liquid becoming faintly yellow. *Salol* (*phenyl salicylate*). 0.25 gram of the sample is boiled with 2 c.c. of aqueous sodium hydroxide, and 20 c.c. of water for some minutes to hydrolyse the compound; when cold, the liquid is diluted to 100 c.c., and 10 c.c. are used for the titration. One mol. of salol requires 10 atoms of bromine.

L. DE K.

Estimation of Hippuric Acid. By WILLIAM ARTHUR CATES (*Chem. News*, 1901, 83, 121).—In using Bunge and Schmeideberg's method for the estimation of hippuric acid, after the washing with alcohol, ethyl acetate, and petroleum, the crystals may advantageously be dissolved in hot water and titrated with *N*/10 sodium hydroxide, using phenolphthalein as indicator; the results are not vitiated by pigmentary matter, and hence are probably more accurate than those obtained gravimetrically.

D. A. L.

Rapid Estimation of Fatty Acids in Soaps. By ACHILLE BAUD (*Ann. Chim. anal. appl.*, 1901, 6, 83—84).—Ten c.c. of the solution of the soap are heated in a graduated tube, having a bulb at the centre and another one at the bottom, with 10 c.c. of hydrochloric acid until the fatty acids are completely liberated. When cold, 35 c.c. of ether are added, the tube is corked and well shaken. When the two layers have completely separated, the volume of the ethereal layer is read off and a definite volume is removed by means of a pipette; the fatty acids are then obtained by evaporating the ether.

L. DE K.

Mean Molecular Weight of the Fixed (Insoluble) Acids of Fats. By MASSIMO TORTELLI and A. PERGAMI (*L'Orosi*, 1901, 24, 1—11).—The authors call attention to the error of the generally accepted view that the index of saponification of a mixture of fatty acids obtained from a fat or oil is identical with the index of acidity. The values of these two quantities have been determined for a large number of mixtures of fatty acids yielded by different fats and oils of various ages, as well as for so-called pure samples of the acids contained in these substances. In nearly all cases differences appear, and on calculating the mean molecular weights of the mixed fatty acids from the two indices, it is found that the number yielded by the saponification index is always less than that given by the index of acidity; the value of the latter often points to a mean molecular weight greater than those of all the component acids of the mixture. It is concluded that the differences thus observed are due to the presence in oils and fats of anhydrides or lactones in a proportion varying with the nature and age of the product. The true mean molecular weight of the fixed fatty acids must hence be deduced from their saponification number determined in the same way as with fats, that is, by hydrolysing with an excess of hot potassium hydroxide, the amount of the excess being

afterwards estimated by titration with a standard mineral acid. Since the proportion of anhydrides or lactones in a fat increases in general with the age of the fat and with the changes which it undergoes, a comparison of the acidity and saponification numbers is useful as an indication of the state of preservation and the freshness of the fat; the better the quality of the latter, the smaller is the difference between the two numbers. That the lactones occurring in oils are not present entirely in the free state, but partly as glycerides, is shown by comparing the oil as found naturally with the same oil after it has been neutralised to remove free fatty acids and washed with absolute alcohol to get rid of lactones in the free state; the proportion of lactones in the oil, as deduced from the difference between the saponification and acidity numbers, is found to be almost exactly the same before and after such treatment. T. H. P.

Use of Amyl Alcohol in the Analysis of Fats. By GEORGES HALPHEN (*Ann. Chim. anal. appl.*, 1901, 6, 133—135).—Referring to the proposal of Eichhorn (this vol., ii, 48), the author reproduces his note in the *Revue Phys. Chim.*, 1899, 295, and claims priority for the use of amyl alcohol for the estimation of free fatty acids in neutral fats. The substance is dissolved in 4—5 vols. of amyl alcohol and the titration made with a solution of sodium hydroxide in 90—95 per cent. alcohol, using phenolphthalein as indicator. The red coloration which indicates the end of the neutralisation is very transient, owing to the rapidity with which saponification commences.

The following method for estimating non-saponifiable substances in fats is rapid, and sufficiently accurate for commercial purposes. Five to ten grams of the fat are dissolved in 10 vols. of carbon disulphide; concentrated sulphuric acid (twice as much as the fat taken) is added drop by drop, with shaking, avoiding rise of temperature; the whole is rinsed into a separating bulb, the lower layer run out, and the upper one shaken with a little animal charcoal to remove tar and traces of acid. It is then filtered, distilled, and the residue weighed. M. J. S.

Estimation of Fat in Blood. By M. BÖNNINGER (*Chem. Centr.*, 1901, i, 583—584; from *Zeit.klin. Med.*, 42, 65—71) See this vol., ii, 325.

Estimation of Fat in Cream. By V. DEHLHOLM (*Exper. Stat. Record*, 1900, 11, 812; from *Mälkeritid*, 1899, 12, 313—319).—The fat is estimated by the Gerber method after diluting the cream with water until the percentage of fat is reduced to about 6—8. The results are slightly low and are corrected by means of a table given in the original papers. The production of froth may be avoided by heating the undiluted cream for 5 minutes at 69°. N. H. J. M.

Estimation of Fat in Milk by means of Anhydrous Sodium Sulphate. By OCTAVE LE COMTE (*J. Pharm.*, 1901, [vi], 13, 58—60).—Twenty grams of anhydrous sodium sulphate are introduced into a mortar, finely powdered and mixed with 10 c.c. of the milk to be tested: if the latter is sour, 1 gram of calcium carbonate is added. After an hour, the sodium sulphate will have completely absorbed the water from the milk, leaving a dry mass which, after being reduced to

a fine powder, is introduced into a tube closed with a plug of cotton wool and extracted with ether.

L. DE K.

Nature and Properties of Corn Oil [Maize Oil]. II. **Determination of the Constitution.** By HERMANN T. VULTÉ and HARRIET WINFIELD GIBSON (*J. Amer. Chem. Soc.*, 1901, 23, 1—8. Compare Abstr., 1900, ii, 697).—Maize oil contains 1.41 per cent. of phytosterol and 1.11 per cent. of lecithin. In addition to the fatty acids detected by previous workers, the authors have identified hypogaecic, arachidic and acetic acids, and have also confirmed the presence of formic acid.

E. G.

Estimation of Unsaponifiable Matters in Commercial Oleins. By PAUL NEFF (*Zeit. angew. Chem.*, 1901, 14, 309—311).—Ten grams of the sample are dissolved in 75 c.c. of 95 per cent. alcohol, 5 grams of potassium hydroxide dissolved in a very little water are added, and the whole is boiled in a reflux apparatus for three-quarters of an hour. The hot liquid is diluted with 50 c.c. of water and transferred to a separating funnel, a few drops of phenolphthalein are added, and the solution nearly neutralised with dilute hydrochloric acid. To the cold liquid are now added 50 c.c. of light petroleum (b. p. not exceeding 80°), and the whole is thoroughly shaken. After a few minutes, the aqueous portion is drawn off, and 25 c.c. of the light petroleum (= 5 grams of sample) are pipetted off and evaporated in a weighed beaker. The residue is dried at 110° and weighed.

The soap solution dissolves a quantity of light petroleum amounting to 9 or 10 c.c., but it appears that it also dissolves a corresponding proportion of unsaponifiable matter; at all events, the results obtained are perfectly trustworthy as shown by a dozen test experiments.

L. DE K.

Detection of Sesamé Oil in Vegetable and Animal Oils. By TAMBON (*J. Pharm.*, 1901, [vi], 13, 57—58).—The reagent consists of a solution of 3 or 4 grams of pure dextrose in 100 c.c. of hydrochloric acid; this solution keeps for a long time without blackening. Fifteen c.c. of the suspected oil are shaken in a glass-stoppered test-tube with 7 or 8 c.c. of the reagent for 2 or 3 minutes, then just heated to boiling and again well shaken. In the presence of 1—5 per cent. of sesamé oil, the liquid after a few minutes assumes a fine rose colour with a violet reflex rapidly turning to a permanent cherry-red. If as much as 10 per cent. is present, the colour appears almost instantaneously.

L. DE K.

Gasometric Estimation of Formaldehyde. By E. RIEGLER (*Zeit. anal. Chem.*, 1901, 40, 92—94).—When hydrazine sulphate is mixed with iodic acid, the whole of the nitrogen is almost instantly liberated. Formaldehydrazone is, however, decomposed much more slowly, so that the amount of formaldehyde which has been added to an excess of hydrazine sulphate can be calculated from the deficiency in the amount of nitrogen liberated by iodic acid, if the measurement is made with sufficient rapidity. The solutions used contain 1 gram of

hydrazine sulphate in 100 c.c., and 5 grams of iodic acid in 50 c.c. of water. The Knop-Wagner azotometer may be used: 20 c.c. of the hydrazine sulphate solution, diluted to 40 c.c., are placed in the outer reaction vessel and 5 c.c. of the iodic acid in the inner tube. After equalising the temperature, the reaction flask is shaken for half a minute, then placed for 2 minutes in the cooling cylinder and the volume of gas noted. A similar quantity of the hydrazine solution is then mixed in a flask with a measured quantity of the formaldehyde solution, containing not more than 0.08 gram of formaldehyde. After a quarter of an hour the mixture is rinsed into the decomposition vessel, and made up to 40 c.c. with the rinsings. The decomposition is performed as before, care being taken that the times specified are not exceeded. One c.c. of nitrogen (at 0° and 760 mm.) = 2.7 mg. of formaldehyde.

M. J. S.

Gasometric Estimation of Acetone in Urine. By E. RIEGLER (*Zeit. anal. Chem.*, 1901, 40, 94—97).—Boiling Fehling's solution oxidises phenylhydrazine with evolution of the whole of its nitrogen in the elementary state (Abstr., 1892, 1322), whilst it has no such action on acetonehydrazone, and this fact has been applied by Jolles to the estimation of acetone. The author simplifies Jolles' process. An alkaline copper solution at the ordinary temperature can be substituted for the boiling Fehling's solution. The solutions used are: (A), 1 gram of phenylhydrazine hydrochloride in 50 c.c. of water; if turbid, the solution should be filtered. (B), Fifteen grams of copper sulphate in 100 c.c. (C), Fifteen grams of sodium hydroxide in 100 c.c.

Fifty c.c. of the urine are mixed with 1 c.c. of glacial acetic acid and distilled into a flask containing 10 c.c. of solution A and 1 gram of crystallised sodium acetate. When 40—45 c.c. have distilled over, the flask is heated for a quarter of an hour on the water-bath, cooled, and its contents rinsed into the evolution flask of a Knop-Wagner azotometer, where they are mixed with 10 c.c. of solution C. In the inner tube are placed 10 c.c. of solution B. After shaking for half a minute and cooling for 5 minutes, the volume of gas can be read off. A similar experiment is made without the acetone, and the difference between the gas volumes (in c.c. at 0° and 760 mm.) multiplied by 2.6 gives mg. of acetone.

M. J. S.

Estimation of Camphor in Camphor Oil. By H. LÖHR (*Chem. Zeit.*, 1901, 25, 292).—The author's process is a purely technical one. The camphor oil is exposed to a low temperature, the camphor is pressed out, and the oil submitted to fractional distillation. The fraction passing over between 195° and 220° is again frozen to recover any camphor it may contain, and the process is then repeated until no more camphor is obtained. With care, the results are almost quantitatively correct.

L. DE K.

Separation and Estimation of Ammonia and Methylamines. By HENRI QUANTIN (*Ann. Chim. anal. appl.*, 1901, 6, 125—126; see Abstr., 1893, ii, 104).—The only new feature in the present paper is the proposal to add a known quantity of methylamine, if the amount

already present is insufficient to maintain the alkalinity of the liquid, during the precipitation of the ammonia as ammonium magnesium phosphate. Methylamine, free from ammonia, may be obtained by distilling a crude methylamine salt with lime into water containing excess of magnesium phosphate. The ammonium magnesium salt, in which the ammonia is to be estimated, must be dissolved in hydrochloric acid before adding soda. M. J. S.

A Simple Ureometer. By FERNAND GIRARDET (*Bull. Soc. Chim.*, 1901, [iii], 25, 329—334).—The apparatus described consists essentially of a vertical tube, connected above with the vessel in which the nitrogen is evolved, which is fixed in the axis of a wider tube, provided at its lower end with a pinchcock and jet. At the commencement of an experiment, the apparatus is nearly filled with water, so as to stand at the same level in the two tubes; the gas is generated in the usual manner with hypobromite, and water is then run out from the wider tube until the level is again equalised. The volume or weight of the water thus collected bears a constant proportion, which is determined once for all, to the volume of nitrogen evolved. The exact proportion depends on the relative diameters of the tubes used; in the apparatus employed by the author it is as 5 to 1. The advantages claimed are ease of construction and great accuracy, without the necessity of graduations. N. L.

Estimation of the Amount of Alkaloids in Cinchona Barks. By B. A. VAN KETEL (*Zeit. angew. Chem.*, 1901, 14, 313—315).—Four grams of the cinchona powder are mixed in a mortar with 2 grams of calcium hydroxide, then moistened with 5 c.c. of ammonia, and boiled in a reflux apparatus with 100 c.c. of ether for half an hour. The solution is filtered, the insoluble matter washed with 80 c.c. of ether, and the filtrate shaken in a separating funnel with 10 c.c. of 10 per cent. hydrochloric acid. The aqueous solution is drawn off and the ether washed with another 5 c.c. of water. The acid solution containing the alkaloids is now shaken with 70 c.c. of ether, and an excess of sodium hydroxide, and then once more with another 50 c.c. of ether; the liberated alkaloids dissolve in the ether, and are recovered by evaporation in a weighed flask. The process may be applied to all drugs which contain non-volatile alkaloids soluble in ether.

L. DE K.

Detection and Estimation of Morphine. By F. WIRTHLE (*Chem. Zeit.*, 1901, 25, 291—292).—Kippenberger has proposed to remove morphine from its solution in fixed alkalis by adding sodium or potassium hydrogen carbonate, and shaking with chloroform containing 10 per cent of alcohol [? by volume]. The author has not been successful with this process, but the morphine may be gradually and completely removed by first acidifying slightly with hydrochloric acid, then rendering alkaline with ammonia, and shaking five or six times in succession with fresh quantities of the chloroform alcohol mixture.

The most delicate test for morphine, and one very useful to ascertain whether the extraction has been complete, is that proposed by Marquis.

The reagent consists of 2 drops of formaldehyde dissolved in 3 c.c. of sulphuric acid ; it gives a fine violet coloration with 0.1 milligram of the alkaloid.
L. DE K.

Estimation of Nicotine in Tobaccos or Tobacco Extracts. By JULES FOTH (*Rev. Intern. Falsif.*, 1901, 14, 12—14).—The tobacco is first dried over quicklime and then ground, powdered, or crushed. Six grams of the dried sample (or 10 grams of the aqueous extract) are mixed in a porcelain dish with 10 c.c. of aqueous sodium hydroxide (20 grams in 100 c.c.) and sufficient plaster of Paris is then added to obtain a dry mass. The mass is transferred to a glass tube 25 cm. long and 5 cm. in diameter, 100 c.c. of a mixture of equal volumes of ether and light petroleum are added, and after inserting a glass stopper the whole is well shaken. After remaining for an hour with occasional shaking, 25 c.c. of the ethereal liquid are pipetted off and introduced into a shaker, and mixed with 40—50 c.c. of water, and a drop of iodo-eosin. Excess of *N*/10 sulphuric acid is added and the liquid then titrated with *N*/10 sodium hydroxide. One c.c. of *N*/10 sulphuric acid neutralised equals 0.0162 gram of nicotine.
L. DE K.

Composition of certain Fruit Juices used in the Preparation of Confectionery, Syrups, &c. By TRUCHON and MARTIN-CLAUDE (*J. Pharm.*, 1901, [vi], 13, 171—176).—Analyses are given of the juice of cherries (early and in season), strawberries (ditto), raspberries, red (unripe) and white gooseberries, peaches, pears, quinces, and apples ; also of the fruit itself (pulp and juice) of apricots, greengages, and yellow plums. Except in the case of peaches and apples which contain also sucrose, the saccharine matter of the above juices is entirely made up of invert sugar, no dextrose being found in any of them. Sucrose also occurs in apricots, greengages and plums.

Of the various natural colouring matters, only that of the peach communicates a yellow-red colour to amyl alcohol when treated in ammoniacal solution, but the colour does not dye silk. None of the natural colouring matters can therefore be mistaken for coal-tar colours.

To detect salicylic acid, the authors proceed as follows. One hundred c.c. of the juice previously diluted with an equal bulk of water are mixed with 2 c.c. of strong ferric chloride, and then with 10 grams of calcium carbonate. The filtrate is agitated with ether and the ethereal residue is then tested as usual with dilute ferric chloride. L. DE K.

Adamkiewicz's Proteid Reaction. By F. GOWLAND HOPKINS and SIDNEY W. COLE (*Proc. Roy. Soc.*, 1901, 68, 21—33).—See this vol., i., 310.

Comparison of Reagents for Milk Proteids with some Notes on the Kjeldahl Method for Nitrogen Determination. By A. VIVIAN (*Exper. Stat. Record*, 1900, 12, 19—20 ; from *Wisconsin Stat. Rep.*, 1899, 179—186).—Cheese is emulsified by rubbing with warm water, acidified with acetic acid, and boiled. Milk is also acidified with acetic acid and boiled. Total nitrogen, and nitrogen not precipi-

tated by acetic acid and heat were determined. Portions of the extracts were treated with zinc sulphate, tannic acid and sodium chloride, and phosphotungstic acid; nitrogen was determined in the filtrates, the precipitated nitrogen being estimated by difference.

The different groups thus determined are as follows:—Insoluble nitrogen (casein, globulin, and albumin); nitrogen in albumoses (total soluble nitrogen less nitrogen in zinc sulphate precipitate); nitrogen in peptones (by tannin, and by phosphotungstic acid); nitrogen in amides (difference between nitrogen in filtrate from phosphotungstic acid and in ammonia); and nitrogen in ammonia.

Cheddar cheese, 6 months old, was found to contain the following amounts of nitrogen:—Insoluble, 3.18; as albumoses, 0.06; peptones by tannin, 0.16; peptones by phosphotungstic acid, 0.13; amides, 0.86; and ammonia, 0.09 per cent.

In determining total nitrogen in cheese, boiling with sulphuric acid must be continued for a considerable time after the solution has become colourless in order to avoid frothing during the distillation. The digestion with acid of the filtrates from milk in the methods above described must be watched closely, and when most of the water has boiled off, the gas must be turned very low for 15—30 minutes. When digested with sulphuric acid, the filtrate from zinc sulphate requires the addition of 0.5 gram of zinc dust, to prevent bumping.

N. H. J. M.

Elimination and Toxicological Detection of Cacodylic Acid.
BY LÉONCE BARTHE and R. PÉRY (*J. Pharm.*, 1901, [vi], 13, 209—214).—The introduction of cacodylic acid into therapeutics has opened up the problem of the detection of the arsenic in this stable compound, with a view to the study of its elimination from the organism. Imbert and Badel evaporate urine with nitric acid, fuse the residue with alkali nitrate and carbonate, and expel the nitric acid by sulphuric acid. The authors find that during the fusion there is generally a cacodylic odour, and always during the subsequent passage of hydrogen sulphide, or the testing with Marsh's apparatus, and quantitative estimations show that the whole of the arsenic is not recoverable from the fused mass, part of the cacodylic acid seeming to escape undecomposed. A distinct odour is obtained when 0.01 mg. of cacodylic acid is introduced into a Marsh's apparatus, whilst 1 mg. mixed with 100 c.c. of urine yields both an arsenical ring and the odour. Elimination commences rapidly, arsenic being detected in the first urine passed after a dose administered by the stomach, but is completed very slowly, arsenic having been found in the urine 70 days after ceasing to take cacodylic acid.

M. J. S.

General and Physical Chemistry.

Refractive Power of the Hydro-derivatives of Cyclic Chains.
By G. PELLINI (*Gazzetta*, 1901, 31, i, 1—18).—Measurements have been made of the refractions of dihydronaphthalene, tetrahydronaphthalene, dihydroanthracene (in benzene), tetrahydrophenanthrene, acenaphthene (in benzene), and acenaphthalene (in benzene). The following table contains the mean experimental numbers for the molecular refractions for the line H_α , together with the calculated values :

| | $M. \frac{\mu_{H_\alpha}^2 - 1}{d}$ | | | $M. \frac{\mu_{H_\alpha}^2 - 1}{(\mu_{H_\alpha}^2 + 2)d}$ | | |
|-------------------------|-------------------------------------|--------|-------|---|-------|-------|
| | Found. | Calc. | Diff. | Found. | Calc. | Diff. |
| Dihydronaphthalene..... | 74·25 | 72·6 | 1·65 | 42·75 | 42·32 | 0·43 |
| Tetrahydronaphthalene.. | 74·05 | 72·8 | 1·25 | 42·94 | 42·62 | 0·32 |
| Dihydroanthracene | 101·82 | 100·00 | 1·82 | 58·70 | 57·88 | 0·82 |
| Tetrahydrophenanthrene | 101·62 | 100·2 | 1·42 | 58·40 | 58·18 | 0·22 |
| Acenaphthene | 94·62 | 85·00 | 9·62 | 53·67 | 49·06 | 4·61 |
| Acenaphthalene..... | 90·08 | 84·8 | 5·28 | 51·64 | 48·76 | 2·88 |

Below are the values of the dispersions for the fundamental nuclei compared with those of their hydro-derivatives :

| | $\frac{\mu_{H\beta} - \mu_{H_\alpha}}{d}$ | $\frac{\mu_{H\beta}^2 - 1}{\mu_{H_\alpha}^2 - 1}$ | | $\frac{\mu_{H\beta} - \mu_{H_\alpha}}{d}$ | $\frac{\mu_{H\beta}^2 - 1}{\mu_{H_\alpha}^2 - 1}$ |
|-------------------|---|---|-------------------------|---|---|
| Naphthalene..... | 0·0297 | 1·0366 | Dihydronaphthalene | 0·0223 | 1·0481 |
| | | | Tetrahydronaphthalene . | 0·01881 | 1·0416 |
| | | | Hexahydronaphthalene { | 0·0158 | 1·0192 |
| | | | | 0·0134 | 1·0198 |
| Anthracene..... | 0·0681 | 1·0887 | Dihydroanthracene. | 0·01615 | 1·0415 |
| Phenanthrene | 0·0452 | 1·2228 | Tetrahydrophenanthrene | 0·01939 | 1·0432 |
| Acenaphthalene.. | 0·03558 | 1·0701 | Acenaphthene | 0·02891 | 1·0580 |

It has been shown that naphthalene and other complex cyclic compounds give values for the molecular refraction much higher than those calculated from the laws of Landolt and Brühl (see Chilesotti, *Abstr.*, 1900, i, 339). The above results show, however, that on passing to the hydro-derivatives of such cyclic compounds, these deviations of the actual from the calculated molecular refractions disappear. This behaviour, which is quite different from that of benzene and its hydrogen additive compounds, is in agreement with the views of Bamberger, who showed (*Abstr.*, 1890, 1299) that the fundamental cyclic nuclei have special chemical properties which are lost on hydro-

genation, the compounds then assuming the properties of benzene derivatives. Thus dihydroanthracene has the two added hydrogen atoms in the middle nucleus, the two lateral nuclei of the anthracene becoming converted into benzene nuclei. Bamberger (*loc. cit.*) has shown that the chemical properties of such compounds are in accord with these views.

A discussion of the various structural formulæ for benzene follows, and the author concludes that, taking into consideration the optical properties alone, the centric formula for benzene and condensed benzene nuclei best explains the observed phenomena. For acenaphthalene and acenaphthene centric formulæ are not possible.

T. H. P.

Spectra of Carbon Compounds By ARTHUR SMITHELLS (*Phil. Mag.*, 1901, [vi], 1, 476—503).—A discussion of the origin of the Swan or hydrocarbon flame spectrum. According to the author, the view which attributes the Swan spectrum to elementary carbon lacks trustworthy experimental support neither has any rational explanation been given of its relation to the line spectrum of carbon. There is evidence also against the view that the Swan spectrum is due to the presence of a hydrocarbon. The theory is advanced that carbon monoxide is the source of the spectrum in question, and this is shown to be consistent with numerous facts, amongst others the direct formation of carbon monoxide in the combustion of carbon and its compounds. This view has been thought inconsistent with the behaviour of carbon compounds under the electric discharge, but the author (who has reinvestigated the spectra of the oxides of carbon) attributes the Swan and oxycarbon spectra to carbon monoxide and carbon dioxide respectively, and shows that on this basis a simple and rational explanation of the facts can be given.

The chief difficulty of the author's theory lies in the cases where the Swan spectrum has been observed in the absence of oxygen; thus it has been found in the electric spectrum of hydrocarbons, of carbon tetrachloride, of cyanogen, and in the spectrum produced by an electric discharge between carbon points in an atmosphere of hydrogen. The author holds that in these cases oxygen and oxygen compounds have not been completely removed, and shows by his own experiments that when a discharge takes place between carbon electrodes in an atmosphere of hydrogen, the Swan spectrum fades as the hydrogen is more thoroughly purified.

J. C. P.

Spectra of Flames resulting from Operations in the Open-Hearth and Basic Bessemer Processes. By W. NOEL HARTLEY and HUGH RAMAGE (*Proc. Roy. Soc.*, 1901, 68, 93—97. Compare Hartley, *Abstr.*, 1895, ii, 432).—Line spectra are not observed in the open hearth furnace, probably because of the oxidising atmosphere. The phenomena of the "basic" Bessemer blow differ considerably from those of the "acid" process. A flame is visible from the commencement of blowing, originating probably from carbonaceous matter in the lining of the vessel. Volatilisation of metal occurs largely at an early period in the blow, and subsequent to this a very large amount of fume is formed, the oxidation of metal and phosphorus producing a

high temperature. The "over-blow" is characterised by a very powerful illumination, accompanied by a dense fume composed of oxidised metallic vapours; the particles must be very minute, for they scatter the light falling on them, and the cloud casts a brown shadow. The spectrum is continuous, but does not extend beyond wave-length 4000. With regard to the spectra of the flames from the first stage of the "basic" process, it is noted that the manganese bands are relatively feeble, and lines of elements, not usually associated with Bessemer metal, are present. Lithium, sodium, potassium, rubidium, and caesium have been traced mainly to the lime; manganese, copper, silver, and gallium to the metal. The intensity of metallic lines (particularly some iron lines) has been observed to vary with the temperature; as the temperature of the flame rises, some lines fade almost entirely, others become stronger. A new potassium line, with wave-length approximately 4642, varies in intensity within rather wide limits. In a given flame, its brilliancy is increased by diminishing the quantity of metallic vapour in the flame, probably owing to the greater freedom of motion thus permitted to the molecules.

J. C. P.

Spark Spectrum of Silicon as rendered by Silicates. By W. NOEL HARTLEY (*Proc. Roy. Soc.*, 1901, 68, 109—112).—In reference to Lunt's paper (Abstr., 1900, ii, 585), the author has re-examined the spectra obtained by him in 1883 from solutions of silicates, but does not find any trace of silicon lines between 4573 and 4553, where Lunt found three. The difference in results is attributed to the different conditions under which the spectra were obtained. The paper contains a table giving the normal length of the six lines in the characteristic group as they are seen when a 1 per cent. (or weaker) solution and graphite electrodes are used.

J. C. P.

Band Spectra of Alumina and Nitrogen. By G. BERNDT (*Ann. Phys.*, 1901, [iv], 4, 788—795).—The band spectrum of aluminium has been attributed by some investigators to the oxide, by others to the metal itself. The author has examined tubes fitted with aluminium electrodes and filled with nitrogen, hydrogen, and oxygen, and concludes that the band spectrum is due to the oxide and not to the metal itself, the presence of oxygen being necessary for its production. In the band spectrum of nitrogen, which has also been investigated, fifteen groups of lines are distinguished, and the wave-lengths of these are communicated in full.

J. C. P.

Absorption Spectra of Chloroanilic and Bromoanilic Acids and their Alkaline Salts. By CARLO FIORINI (*Gazzetta*, 1901, 31, i, 33—39).—The author has made comparative measurements of the absorption spectra and electrical conductivities of chloroanilic and bromoanilic acids, and of their alkali-salts. A Hüfner-Albrecht spectrophotometer was employed, the coefficient of extinction ϵ being obtained by means of the rotation of an analysing nicol. The numbers obtained show that the small colour intensity of the salts corresponds with a high degree of dissociation, whilst in the case of the acids a high colour intensity corresponds with a much lower dissociation. It is

hence the non-dissociated molecules which principally contribute to the colour, the ions being much less coloured. It is not possible, however, to calculate the ratio between the colouring powers of the non-dissociated molecules and of the ions. T. H. P.

Theory of Colour Shade. By CARL LIEBERMANN (*Ber.*, 1901, 34, 1040—1042).—The author calls attention to the fact that by the introduction of hydroxyl groups the red colour of alkaline solutions of aurin becomes changed into the blue-black of hexahydroxyaurin, and similarly the red colour of rosaniline becomes converted into the blue of hexahydroxyrosaniline. The replacement of the hydrogen of the hydroxyl groups by methyl has little effect on the shade of colour. Numerous examples are quoted to show that entrance of hydroxyl groups into a colouring matter brings about a change of tint in the order: yellow \rightarrow orange \rightarrow red \rightarrow violet \rightarrow blue \rightarrow black. The position as well as the number of hydroxyl groups is of importance, as is illustrated by the colours of alkaline solutions of the various hydroxyanthraquinones. The azo- and amino-groups exert a similar influence, whilst the sulphuryl group does not. K. J. P. O.

A New Method of testing colourless Carbon Compounds for Absorption of Light. By JOHANNES PINNOW (*J. pr. Chem.*, 1901, [ii], 63, 239—240).—The method outlined in this preliminary notice is based on the observation that substances known to be affected by light have the power of diminishing the fluorescence of β -naphthylamine, anthracene, quinine sulphate, acridine sulphate, and fluorescein; conversely, substances which produce a diminution of fluorescence are decomposed by light. J. C. P.

Researches on Standard Cells, especially the Weston Cadmium Cell. By WILHELM JAEGER and STEPHAN LINDECK (*Ann. Phys.*, 1901, [iv], 5, 1—50).—The ratio of the *E.M.F.*'s of a large number of Clark and Weston cells has been determined, and the results confirm earlier investigations. Cadmium cells with 14.3 per cent. amalgam exhibit irregularities in the neighbourhood of 0°, but are quite regular from 10° upwards. It is better to use 12 or 13 per cent. amalgam in the cadmium cells; these show no irregularity even at 0°, and are therefore admirably suited for use as standards. The authors' results are at variance with those of Cohen (*Abstr.*, 1900, ii, 702; this vol., ii, 142. Compare also Jaeger and Lindeck, *Abstr.*, 1900, ii, 703). J. C. P.

Irregularities of the Cadmium Standard Cell. By C. H. WIND (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 595—601).—Many of the irregularities observed in the behaviour of Weston cadmium cells (see Jaeger and Wachsmuth, *Abstr.*, 1897, ii, 86; Jaeger, *Abstr.*, 1898, ii, 364; Kohnstamm and Cohen, *Abstr.*, 1898, ii, 495; Cohen, *Abstr.*, 1900, ii, 702; this vol., ii, 142; Jaeger and Lindeck, *Abstr.*, 1900, ii, 703; preceding abstract) may be explained by the existence of two phased equilibria in the cadmium amalgam, and by retardations in the attainment of the equilibria. The recommendation of the Physikalisch-Technische Reichsanstalt that an amalgam with less than 14.3 per cent. of cadmium should be used, insures a cell with a perfectly

definite *E.M.F.*, and makes the cadmium cell more serviceable as a standard. J. C. P.

Pyrogenic Daniell Cells. By R. SUCHY (*Zeit. anorg. Chem.*, 1901, 27, 152—198).—The *E.M.F.* of cells of the Daniell type containing fused salt instead of solution have been determined over a wide range of temperature. The cell was either of the U-shaped type used by Weber (Abstr., 1899, ii, 724) or, to further prevent diffusion, the fused salts and the metal regulus were contained in closed tubes pierced near the top with a small hole and immersed in a bath of one of the fused salts. This bath was heated by a special furnace, whereby the temperature (measured by a Le Chatelier pyrometer) was maintained constant. The results obtained at temperatures above 520° were:

| Cell. | | <i>E.M.F.</i> |
|---|-------|---|
| Pb PbCl ₂ AgCl Ag | | 0.349 - 0.000361 (<i>t</i> - 520°) volt. |
| Pb PbCl ₂ KCl + LiCl AgCl Ag | | 0.339 - 0.000357 (<i>t</i> - 520°) „ |
| Zn ZnCl ₂ PbCl ₂ Pb | | 0.276 - 0.000096 (<i>t</i> - 520°) „ |
| Zn ZnCl ₂ AgCl Ag | | 0.496 volt at 520° |
| | | 0.339 „ at 680°. |

Lorenz (Abstr., 1900, ii, 61) concludes that the *E.M.F.* of a cell $M_1 | M_1X | M_2X | M_2$ should be equal to the difference of the *E.M.F.* of $M_1 | M_1X | X$ and $M_2 | M_2X | X$. In order to institute a comparison, the *E.M.F.* of the following simple cells were also determined:

| Cell. | | <i>E.M.F.</i> |
|--|-------|--|
| Zn ZnCl ₂ Cl ₂ | | 1.662 - 0.000751 (<i>t</i> - 430°) volts. |
| Ag AgCl Cl ₂ | | 0.902 volt at 480°. |
| | | 0.842 „ at 670°. |

If we take account also of Weber's (*loc. cit.*) measurement of the *E.M.F.* of the cell $Pb | PbCl_2 | Cl_2 = 1.282 - 0.000584 (t - 506)$ volt, we find that denoting $M_1 | M_1X | X$ by E_1 , $M_2 | M_2X | X$ by E_2 , and $M_1 | M_1X | M_2X | M_2$ by E , the difference $E_1 - E_2$ is not equal to E , as Lorenz concludes it should be. Instead, it is invariably higher, that is, $(E_1 - E_2) - E$ has a positive value. From these differences the author calculates, on the assumption that the *E.M.F.* of the liquid cell formed by the two fused salts is negligible, the ratio of the ionic concentrations of the metals to be:

$$C(\text{Ag})/C(\text{Pb}) = 3.2 : C(\text{Pb})/C(\text{Zn}) = 2.2 : C(\text{Ag})/C(\text{Zn}) = 60.2.$$

This third value, when calculated from the first two, amounts only to 7.0, and this disparity shows that the liquid cell referred to cannot be neglected, and herein there is a perfect analogy between Daniell cells with fused salts and those with solutions. The analogy between the two is strengthened by the fact that by diluting the salt at the cathode the *E.M.F.* gradually sinks, becomes zero, and ultimately changes sign, just as in ordinary solution cells.

From measurements with the cell $Pb | PbCl_2 | AgCl | Ag$, in which the concentration of the AgCl was varied, it has been possible to arrive at the degree of dissociation of fused silver chloride at high temperatures; $\alpha(520^\circ) = 0.17$, $\alpha(640^\circ) = 0.28$, $\alpha(730^\circ) = 0.60$. J. McC.

[**E.M.F. of Concentration Cells.**] By WALTHER NERNST (*Zeit. physikal. Chem.*, 1901, 36, 596—604).—A reply to criticisms of Arrhenius, Kohnstamm, Cohen, and Noyes. It is shown that the expression for the *E.M.F.* of a concentration cell given by Arrhenius (this vol., ii, 144) is identical with that of the author to which Arrhenius objects (see also Jahn, this vol., ii, 299). Other criticisms of various authors are also replied to or discussed. L. M. J.

Capillary-electrical phenomena. By WILHELM PALMAER (*Zeit. physikal. Chem.*, 1901, 36, 664—680).—The paper contains a discussion of the theories of Helmholtz, Warburg, and Nernst, regarding electrocapillary phenomena, in which the author considers that there is no evidence to support Helmholtz's view of the influence of time or to support Warburg's idea of the capability of mercury to cause a condensation of the solution at its surface. Further, the explanation of Warburg would necessitate an inconceivably high concentration of the salt in the layers of solution contiguous to the mercury. The Nernst theory explains most of the facts without the necessity of any new hypothesis, both in regard to the phenomena obtained with pure mercury and with amalgams, whereas Warburg's theory necessitates contradictory suppositions with different amalgams. (Compare Abstr., 1898, ii, 276). L. M. J.

Rate of Electrolytic Deposition of Copper in Presence of Sulphuric Acid. By JOS. SIEGRIST (*Zeit. anorg. Chem.*, 1901, 26, 273—321).—When a solution of copper sulphate in sulphuric acid of maximum conductivity (sp. gr. 1.225 at 15°) is electrolysed at constant temperature, a constant current and platinum electrodes being used and the solution well stirred, the rate of deposition of copper, dx/dt , is proportional to the current (as is required by Faraday's law) so long as the concentration exceeds a certain value, or, expressed in symbols, $dx/dt = k \dots (1)$, where k is a constant. As the concentration diminishes, the rate of deposition becomes smaller, and finally becomes proportional to the concentration of the copper sulphate, $dx/dt = k'(a - x) \dots (2)$, where a is the initial concentration of the copper, x the quantity deposited, and k' another constant having a smaller value than k in equation (1). Between the concentrations at which equations (1) and (2) hold good, there is a series of concentrations for which $dx/dt = k''(a - x)^n$, k'' having values between k and k' , and n passing through all values between 0 and 1.

The value of k' in equation (2) is much affected by, and increases with, the rate of stirring; it is also proportional to the temperature, and increases as the current density diminishes. T. E.

Amphoteric Electrolytes and Internal Salts. By K. WINKELBLECH (*Zeit. physikal. Chem.*, 1901, 36, 546—595).—Many weak electrolytes exhibit both acidic and basic characters, for example, many metallic hydroxides, the oximes, and amino-acids. Such compounds are termed amphoteric, and the cause of the peculiarity lies most probably in the capability of forming, or of combining with, either hydrogen or hydroxyl ions. The author has determined the hydrogen and the hydroxylic dissociation for a number of such compounds, em-

ploying both the conductivity method used by Walker (Abstr., 1890, 5) and the method of hydrolysis due to Shields (Abstr., 1893, ii, 448). The compounds investigated were betaine (hydroxylic dissociation only), sarcosine, leucine, glycine, alanine, taurine, asparagine, *o*-, *m*-, and *p*-aminobenzoic acids, aspartic acid, and (hydrogen dissociation only), hippuric, sulphanilic and sulphamic acids. No clear connection appears to exist between the acidic and basic characters, thus in the series, alanine, glycine, leucine, sarcosine, betaine, the hydrogen and hydroxylic dissociation decrease together, whilst the same obtains in the case of the aminobenzoic acids. For sulphamic, sulphanilic, and hippuric acids, however, where the hydrogen dissociation is considerably greater, the hydrolytic dissociation is exceedingly small, and was not measured. The acid of methyl-orange was also examined and found to be considerably stronger than carbonic acid; hydrocyanic acid exhibits no basic function; hydroxylamine was found to be a fairly strong base and to possess only very slight acid properties, whilst no acidity was found in the case of carbamide. If the amino-acids are regarded as internal salts, they are capable of being hydrolysed by water just as other salts of weak acids with weak bases, that is, the water can, as a weak base or weak acid, form undissociated salts with the acid or basic group.

L. M. J.

Relation between the Dissociation Constant and the Degree of Dissociation of an Electrolyte in the presence of other Electrolytes. By YUKICHI ŌSAKA (*Zeit. physikal. Chem.*, 1901, 36, 539—542).—The author, by consideration of the dissociation in the case of a system of electrolytes in solution, obtains the following result. The degree of dissociation of a very weak electrolyte is equal to its dissociation constant divided by the total concentration of all the anions or cations in the solution. This conclusion had been previously stated by Arrhenius, but without a general proof.

L. M. J.

Pyrogenetic Reactions induced by the Electric Current. By WALTHER LÖB (*Ber.*, 1901, 34, 915—918).—Water, when heated by an electric arc generated between carbon poles, interacts with this element yielding a mixture of hydrogen, carbon monoxide, carbon dioxide, and small quantities of saturated and unsaturated hydrocarbons. Methyl alcohol, when similarly treated, gives rise to methane, hydrogen, and formic acid, together with traces of acetylene and the oxides of carbon; formaldehyde could not, however, be detected among the products of decomposition. Acetic acid furnishes hydrogen, saturated and unsaturated hydrocarbons, and the oxides of carbon. The gas produced by the decomposition of benzene and naphthalene consists chiefly of hydrogen, the liquid products are contaminated by separated carbon and yield no definite compounds. These results are obtained both with direct and alternating currents and the products of decomposition are the same, whether the substance under treatment is in the liquid or the gaseous state. When methyl alcohol is maintained in contact with a wire heated to redness by the electric current, it decomposes, yielding hydrogen, carbon monoxide, methane, and formic acid, together with traces of trioxymethylene and carbon dioxide. Under these conditions,

benzene gives rise to diphenyl and a hydrocarbon of higher melting point, probably diphenylbenzene, aniline undergoes condensation forming diphenylamine and carbazole with the elimination of ammonia, and nitrobenzene is decomposed into nitric oxide and a solid compound not yet characterised. G. T. M.

Generalisation of Trouton's Law. By ROBERT DE FORCRAND (*Compt. rend.*, 1901, 132, 878—882).—It has been shown by Le Chatelier and Matignon (*Abstr.*, 1899, ii, 273) that a relation similar to Trouton's law holds for many dissociable compounds, that is, that the heat of formation divided by the temperature at which the dissociation pressure is 760 mm. gives values which vary from 23 to 32, being in most cases about 30. The case of dissociation is not, however, completely analogous to the evaporation, alone considered in Trouton's law, as it involves the formation of a gas from a solid, and the author states that if the heat of fusion is added to the heat of vaporisation for the determination of Trouton's constant, the quotient then obtained agrees with that found for dissociation. The law may hence be generalised thus: In chemical or physical changes, the heat of solidification of any gas is proportional to its temperature of vaporisation under atmospheric pressure. This is stated to be valid for carbon dioxide, ammonia, water, glycol, chlorine, bromine, iodine, phenol, benzene, naphthalene, ethylene dibromide, methyl oxalate, and formic, acetic, and butyric acids, the quotients only varying between 28 and 32. L. M. J.

Modification of Landsberger's Apparatus for the Determination of the Elevation of the Boiling Point. By C. N. RIIBER (*Ber.*, 1901, 34, 1060—1064).—Landsberger's apparatus (*Abstr.*, 1898, ii, 283) has been modified in such a manner that the vapour of the solvent, after leaving the tube containing the solution, passes into a condenser so arranged that the condensed liquid can flow back into the flask. The advantages of this method are that much less solvent is required, that a slight impurity in it exerts very little influence since the liquid in the flask has always the same composition, and consequently the composition and temperature of its vapour are constant, and that no interruption of the boiling is necessary. The results of a number of determinations are appended. For details of the method, the description and diagram in the original must be consulted. E. G.

Vaporisation of Binary Mixtures. By PIERRE DUHEM (*Zeit. physikal. Chem.*, 1901, 36, 605—606).—A reply to Kohnstamm (this vol., ii, 145), in which it is pointed out that the theory of Van der Waals is quite insufficient in the case of binary mixtures, as is evident from the recent work of Caubet (this vol., ii, 147). L. M. J.

Vapour Pressure of Ternary Mixtures. By FRANZ A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1901, 36, 710—740).—A continuation of the previous papers (this vol., ii, 224, 305; compare this vol., ii, 146) in which the effect of pressure and, briefly, of temperature, on the course of the vaporisation and condensation curves are considered. L. M. J.

Cryoscopic Researches. By PAUL CHRUSTSCHOFF (*Compt. rend.*, 1901, 133, 955—957).—The author adds details of the apparatus and of the method of observation by which the results previously recorded were obtained (this vol., ii, 86). L. M. J.

Cryoscopic Experiments with the Bromides of Arsenic and Antimony. By FELICE GARELLI and VITTORIO BASSANI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 255—262. Compare Tolloczko, *Abstr.*, 1900, ii, 190; *Bull. Acad. Sci. Cracow*, 1901, 1).—For the determination of the molecular depressions of the freezing points, cryoscopic measurements were made of benzene, bromoform, iodine, arsenic tri-iodide and trichloride, stannic iodide, antimony chloride and bromide in arsenic bromide solution and of diphenyl, diphenylmethane, bromoform, antimony chloride, arsenic tri-iodide and tribromide in antimony bromide. The following conclusions are drawn.

The mean molecular freezing point depression for arsenic bromide is 194.2, which agrees well with the value given by Raoult's empirical rule, namely, 195.3. Tolloczko (*loc. cit.*) gave 206.

Solutions of antimony chloride in arsenic bromide give freezing point depressions much less than the theoretical, a fact ascribed by the authors to the formation of solid solutions. Tolloczko also found small depressions for solutions of arsenic bromide in antimony chloride, and he supposed that either dissociation or a chemical action such as $\text{AsBr}_3 + \text{SbCl}_3 = \text{AsBr}_2\text{Cl} + \text{SbCl}_2\text{Br}$, takes place. This explanation is untenable in the light of the author's observations. The small depressions obtained by Tolloczko for solutions of arsenic chloride in antimony chloride are probably also due to the analogy in constitution existing between the solvent and solute.

Anomalous values are also obtained for mixtures of the bromides of arsenic and antimony, and are evidently due to the formation of isomorphous mixtures.

Tolloczko (*loc. cit.*) corrects the number, 280, given by Garelli (*Abstr.*, 1899, ii, 271) for the molecular freezing point depression of stannic bromide, giving the value 306. The authors point out that both from the results of Tolloczko and those of Garelli, the latter number is probably high, whilst 280 agrees well with the value given by Raoult's rule, the melting point and latent heat of fusion leading to the number 260. T. H. P.

Determination of the Calorific Power of Fuels. By ORAZIO REBUFFAT (*Gazzetta*, 1901, 31, i, 78—82).—The author briefly considers the various methods for the determination of the calorific power of fuels, and criticises the recent publication of Antony and di Nola (this vol., ii, 6) on Berthier's method. Under the conditions stated by these authors, only a portion of the available hydrogen of the fuel takes part in the reduction of lead fluoride; the latter also reacts readily with sulphur and with compounds of silica. The experiments of von Jüptner (*Oester. Zeit. Berg. Hutt.*, 1893), which are not mentioned in Antony and di Nola's paper, are also referred to.

In order to obtain accurate numbers for the calorific values of fuels, it is necessary to make use of the calorimeter or the calorimetric bomb,

with which compressed oxygen is conveniently employed. Some commercial oxygen is produced by an electrolytic process, and so contains small proportions of hydrogen, which must be allowed for.

T. H. P.

Relation of the Viscosity of Mixtures of Solutions of Certain Salts to their State of Ionisation. By JAMES BARNES (*Trans. Nov. Scot. Inst. Sci.*, 1900, 10, 113—128).—The viscosity of mixtures of dilute salt solutions can be calculated from the formula: $P = Pw + 1/p[(k_1(1 - a_1)n_1 + l_1a_1n_1) \cdot v_1/(v_1 + v_2) + (k_2(1 - a_2)n_2 + l_2a_2n_2) \cdot v_2/(v_1 + v_2)]$, deduced by Macgregor (*Trans. Nov. Scot. Inst. Sci.*, 1896—1897, 9, 219), where Pw is the viscosity of water, k and l the ionisation constants, a the ionisation coefficients, and n the concentrations of the electrolytes, v the volumes of the constituent solutions, and p the ratio of the volumes of the solutions after and before mixing.

Applied to mixtures of potassium and sodium chlorides, potassium and barium chlorides, potassium and sodium sulphates, and potassium and copper sulphates, this formula leads to values which agree well with the viscosities found by Kanitz (*Abstr.*, 1897, ii, 308).

J. McC.

Employment of the Method of counting Drops for the Measurement of Surface Tensions. By PHILIPPE A. GUYE and F. LOUIS PERROT (*Arch. Sci. Phys. Nat. Geneva*, 1901, [iv], 11, 225—265, 345—388).—The authors accurately confirm the fact that the weight of a falling drop depends on the time taken for its formation. The method of falling drops gives results for the surface tension of organic liquids which agree with the more accurate values obtained by Ramsay and Shields (*Trans.*, 1893, 63, 1089) to within 1—2 per cent. This precision is quite sufficient when the observations are made with the view of determining the molecular association of a liquid, and the method may become of practical importance in physical chemistry. The authors describe an improved apparatus for carrying out the measurements at different temperatures, in which a certain number of drops are weighed, or the drops occupying a certain volume are counted.

J. McC.

Does a Law corresponding with that of Avogadro hold for the Solid State? Hardness of Metals and Alloys. By CARL BENEDICKS (*Zeit. physikal. Chem.*, 1901, 36, 529—538).—It was shown by Bottone (this Journ., 1875, 232) that in a series of 21 metals the hardness was proportional to the specific gravity and inversely proportional to the atomic weight, that is, was proportional to the atomic concentration. The later values of Rydberg (*Abstr.*, 1900, ii, 392) for the hardness of elementary substances according to Mohs' scale, also confirm the above generalisation. A few examples of various alloys are also used to deduce the law that the hardness of solid solutions increases with increase of osmotic pressure.

L. M. J.

Theory of Capillarity. By G. BAKKER (*Zeit. physikal. Chem.*, 1901, 36, 681—692).—An extension of previous mathematical papers (*Abstr.*, 1900, ii, 466; this vol., ii, 88), in which the author deduces

expressions connecting the molecular pressure and surface tension ; and further derives and discusses the Laplace expression.

L. M. J.

The "Myriotone" as Unit in Osmotic Measurements. By LEO ERRERA (*Bull. Acad. Roy. Belg.*, 1901, 3, 135—153).—The author proposes to term the pressure of one dyne per square centimetre a "tone" and to use the myriotone (= 10,000 tones) as the unit in gas and osmotic measurements. One myriotone is approximately equal to 1/100 atmosphere. When v is measured in litres and p in myriotones the constant R of the equation $pv = RT$ is equal to 8.32.

The symbol for the myriotone is \bar{M} .

J. McC.

Extent to which the Interaction of Ionic Charges diminishes the Osmotic Pressure. By VL. VON TÜRIN (*Zeit. physikal. Chem.*, 1901, 36, 524—528).—An extension and elucidation of the author's previous communication (Abstr., 1900, ii, 712).

L. M. J.

Etard's Law of Solubility. By ERNST COHEN and E. H. BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 561—565).—According to Etard (*Ann. Phys. Chem.*, 1898, [ii], 65, 344), the curves representing the solubility of salts as a function of the temperature are straight lines, provided the solubility be defined as the weight of salt in 100 grams of the saturated solution. The authors show from the work of various investigators that Etard's law is not in accordance with facts.

J. C. P.

Aqueous Solutions of Double Salts. IV. Iodides, Cyanides, Nitrates, and Sulphates. By HARRY C. JONES and B. PALMER CALDWELL (*Amer. Chem. J.*, 1901, 25, 349—390).—A continuation of previous work (Jones and Mackay, Abstr., 1897, ii, 396 ; Jones and Ota, Abstr., 1899, ii, 587 ; Jones and Knight, Abstr., 1899, ii, 628. Compare Lindsay, this vol., ii, 143). Study of the electrical conductivity shows that the double iodides of strontium and cadmium, and potassium and cadmium exist largely undecomposed in concentrated solution, breaking down more and more as the dilution increases. The same holds for the double nitrates of ammonium with praseodymium and neodymium, and for the double cyanide of potassium and mercury. The nitrates, however, break down at a comparatively early stage of dilution. The double sulphates of ammonium with cadmium, copper, magnesium, iron, nickel, and the double sulphate of potassium and nickel remain partly undissociated in concentrated solution, and even in dilute solution are not entirely broken down into their constituents.

Cadmium sulphate, potassium cadmium iodide, praseodymium nitrate, and ammonium praseodymium nitrate are substances whose molecular lowering of the freezing point of water does not increase regularly with the dilution ; there exists a well-defined minimum of the molecular depression, in each case about the concentration 0.2 normal.

J. C. P.

Measurement of the Work done by Affinity. By ERNST COHEN [and A. W. VISSER] (*Zeit. physikal. Chem.*, 1901, 36, 517—523).—Under the above title, van't Hoff, in the *Études de dynamique Chimique*, calculates the heat evolved by the conversion of the second system into the first in the equilibrium $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{MgSO}_4 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{FeSO}_4 \cdot 6\text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, employing the values for the vapour tension of the salts which were obtained by Wiedemann. As, however, these values are certainly inaccurate and do not agree with the later observations of Frowein (Abstr., 1888, 337), the authors have redetermined them at temperatures from 30° to 48°, employing Frowein's method. The value at 40° for the heat of hydration of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is calculated as 3712 cal., agreeing well with Thomson's calorimetric value, 3700; the heat of hydration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was calculated as 1912 cal., and the vapour pressure of the iron salt is greater than that of the magnesium salt, so that the change is in the opposite direction to that stated by van't Hoff. The heat of transition at 40.02° is 1800 cal., the transition point 46.5°, and the work which can be performed owing to affinity, being $q(P - T)/P$ where P is the transition temperature, reduces to $1800 - 5.632 T$.
L. M. J.

Theory of Catalytic Reactions. By HANS EULER (*Zeit. physikal. Chem.*, 1901, 36, 641—663).—See Abstr., 1900, ii, 532.

Velocity and Catalysis in Heterogeneous Systems. By K. DRUCKER (*Zeit. physikal. Chem.*, 1901, 36, 693—709).—The formula of Noyes and Whitney for the rate of dissolution of a solid in its own solution is insufficient, as it does not take into account the volume of the solution (Abstr., 1897, ii, 479), and the author deduces a formula of more extended applicability in which the velocity of dissolution is a function of the volume, its validity being indicated by experiments with barium hydroxide. The experiments of the author on the rate of solution of arsenious oxide in the presence of various acids are also considered (this vol., ii, 230). The rate of dissolution differs but little for the two acids, hydrochloric and sulphuric, and is approximately proportional to the square root of the H^+ concentration; the effect of HO^+ ions is more marked, but the same proportionality obtains. The formula of Noyes and Whitney for the rate of dissolution was not found to be valid, as the velocity, until very near the saturation concentration, was not dependent on the concentration of the arsenious oxide in the solution, but only on that of the catalysing acid.
L. M. J.

Equilibrium between the different Stages of Oxidation of the same Metal. By EMIL ABEL (*Zeit. anorg. Chem.*, 1891, 26, 361—437).—Two classes of equilibria between the ions of the same metal possessing different valency are distinguished. In the first class, the metal is in contact with the solution containing the ions and the reaction which occurs is represented by the equation, (1), $nM^{(m)} + (m - n)M \rightleftharpoons mM^{(n)}$, where M , $M^{(m)}$ and $M^{(n)}$ represent respectively the neutral metal and the ions with m and n charges of electricity (m is supposed to be greater than n). Since the active

mass of the solid metal is constant, we have in equilibrium $[M^{(m.)}]^n/[M^{(n.)}]^m = \text{constant}$, where the expressions in square brackets represent the concentrations of the ions. The second class of equilibria is characterised by the presence of the undissolved, electrically neutral substance furnishing the anion. When A' represents a univalent anion, and A the neutral substance, the reaction is represented by the equation, (2), $M^{(m.)} + (m-n)A' \rightleftharpoons M^{(n.)} + (m-n)A$, and in equilibrium $[M^{(m.)}][A']^{m-n}/[M^{(n.)}] = \text{constant}$. Equations are also obtained representing the potential difference between a metal and a solution containing m - and n -valent ions in equilibrium for which the original must be consulted.

From equation (2) it follows that as the concentration of the m -valent ions is increased that of the n -valent ions is increased also, and that finally a point may be reached at which the solubility product of the salt corresponding with the lower (n -valent) stage of oxidation is attained. This salt then separates out as a solid and any attempt to further increase the concentration of the m -valent ions merely increases the quantity of the solid salt. If this point is reached before the solubility product of the m -valent salt has been exceeded, it will not be possible to prepare this salt in the solid state (from aqueous solutions).

The experimental part of the paper deals with salts of mercury and copper.

Solutions of mercuric nitrate in 0.3*N* nitric acid are shaken with mercury until equilibrium is attained and the concentrations of the mercurous and mercuric salts in the solution determined. These concentrations may be taken to be nearly proportional to the concentrations of the corresponding ions. The ratio $[\text{HgNO}_3]/[\text{Hg}(\text{NO}_3)_2]$ is found to be constant and equal to 239.5 at 25°. This shows that the two ions have the same valency and that the reaction therefore takes place in accordance with the equation $\text{Hg}^{++} + \text{Hg} = \text{Hg}^+ - \text{Hg}^+$, the mercurous ion consisting of two atoms.

Phenomena such as the non-existence of mercurous cyanide and sulphide, the formation of mercuric chloride and mercury by boiling calomel with hydrochloric acid or a solution of potassium chloride, &c., are shown to be explained by the equilibrium between the mercurous and mercuric ions.

When an acid solution of cupric sulphate is shaken with copper (in absence of oxygen) some of the metal is dissolved, cuprous sulphate being formed. When this solution is electrolysed, the quantity of copper deposited at the cathode is very slightly in excess of that which would be deposited if nothing but cupric ions were discharged. From a solution containing cupric and cuprous ions in equilibrium, the two kinds of ions should, according to Nernst, be deposited in proportion to their concentrations. Calculating the concentration of the cuprous ions on the assumption that the cuprous salt is normally dissociated, the excess of copper deposited by electrolysis would be from 8 to 20 times that actually found. It follows, therefore, that cuprous sulphate is dissociated to an abnormally small extent, probably owing to the formation of complex ions.

The velocity of reaction between copper and an acid cupric sulphate solution increases rapidly with the temperature. Equilibrium is best

attained by heating the solution with copper at 100° and then allowing it to cool at the required temperature, when copper crystallises out. For solutions of cupric sulphate in normal sulphuric acid, it is found that the expression $\sqrt{[\text{CuSO}_4]/[\text{Cu}_2\text{SO}_4]}$ is constant at constant temperature, $[\text{CuSO}_4]$ and $[\text{Cu}_2\text{SO}_4]$ being the concentrations of the cupric and cuprous sulphates in equilibrium in gram-molecules per litre. The values of the constants are: 82.4 at 100° , 136.7 at 40° , 157.2 at 25° , and 317.7 at 0° . From this it follows that the complex cuprous ion is univalent and that the reaction is represented by the equation $\text{CuSO}_4 + \text{H}_2\text{SO}_4 + \text{Cu} = 2\text{HCuSO}_4$. Silver sulphate behaves in a similar way, as is shown by the fact that it is more soluble in solutions of sulphuric acid or of alkali sulphates than in pure water. If the solution of cupric sulphate is insufficiently acid, cuprous oxide separates out, since, owing to the greater concentration of the OH ions, the small solubility product of this compound is soon reached.

Determinations of the solubility of cuprous chloride in hydrochloric acid lead to the conclusion that complex ions are formed, the greater part of which possess the formula Cu_2Cl_4 , the equation being $2\text{HCl} + \text{Cu}_2\text{Cl}_2 = \text{H}_2\text{Cu}_2\text{Cl}_4$. In conformity with this conclusion, it is found that the freezing point of hydrochloric acid is raised when cuprous chloride is dissolved in it.

Since the small quantity of cuprous salt which can exist in equilibrium in a solution of cupric sulphate is, for the greater part, present in the form of a complex ion, it follows that the ratio between the concentration of cupric and cuprous ions in equilibrium must have a very large value. Colourless solutions of cuprous salts (which contain practically no cupric ions) must therefore contain almost immeasurably small quantities of cuprous ions, and the cuprous copper in such solutions must exist in the form of complex ions. A cuprous salt which could dissolve appreciably in water and which could undergo normal electrolytic dissociation would at once decompose into a cupric salt and copper; the non-existence of cuprous nitrate is explainable in this way. The cuprous salts known are all practically insoluble in water. The impossibility of preparing solid cuprous sulphate from aqueous solution is explained similarly.

The paper concludes with an account of a careful investigation of the copper voltameter, more especially with small current densities, the principal results of which are:

When a solution of copper sulphate which has been treated with copper until equilibrium is attained is electrolysed in an atmosphere of hydrogen or nitrogen with a small current density, the increase of weight of the cathode is smaller and the decrease of weight of the anode greater than would theoretically be anticipated. The differences depend on the concentration of the sulphuric acid used.

A dissolution of the electrodes appears to take place which may be due to a reduction of the sulphuric acid present, which gives rise to the formation of more complex cuprous ions, owing to which equilibrium is disturbed and further quantities of copper are dissolved.

The separation of the electrodes by a capillary tube or by a porous diaphragm and a preliminary electrolysis of the solution with a weak current eliminate the errors above-mentioned almost completely.

The results obtained with the copper voltameter are more exact at low temperatures than at higher ones. T. E.

Chemical Energy of Formic Acid. Displacement of the Nitric Acid of Nitrates by Formic Acid. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1901, [iii], 25, 427—428).—The heat of neutralisation of formic acid by bases is less than that of nitric acid, but nevertheless the former is capable of displacing the latter, as is shown by the red coloration produced when concentrated formic acid is added to a mixture of a nitrate with brucine. A similar reaction is given on heating, although less readily, by acetic, propionic, butyric, and valeric acids. The reaction is regarded as an instance of the limitation of the principle of maximum work. N. L.

The Standard of Atomic Weights. By HUGO ERDMANN (*Zeit. anorg. Chem.*, 1901, 27, 127—137. Compare this vol., ii, 231).—A polemical article in reply to Brauner, in which the author supports as standard $H = 1$. Out of 129 replies to the circular addressed to the university teachers in Germany, Austria, and Switzerland, 105 were in favour of $H = 1$, whilst only 20 supported $O = 16$. J. McC.

Report of the [American] Committee on Atomic Weights. By FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1901, 23, 90—95).—A résumé of the work published during 1900 on the atomic weights of nitrogen, iron, calcium, gadolinium, thorium, yttrium, samarium, helium, neon, argon, krypton, xenon, and radium; a corrected table of the atomic weights of all the elements is appended. E. G.

Simple Reflux Apparatus. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1901, [iii], 25, 476—479).—A flask of cold water, or a Wurtz flask through which water circulates, placed in a funnel fixed in the cork of the distilling flask forms a cheap reflux apparatus in which caoutchouc joints and the risk of loss by spiriting are avoided. In the case of very volatile liquids, the funnel is fitted into a long-necked bulb tube surrounded by a spiral of lead tubing through which water circulates. Illustrations of the apparatus are given in the paper. N. L.

Inorganic Chemistry.

Liquefaction of Hydrogen. By MORRIS W. TRAVERS (*Phil. Mag.*, 1901, [vi], 1, 411—423).—A description of the apparatus employed for the production of the liquid hydrogen which has been used by Ramsay and the author (this vol., ii, 237) in the separation of neon and helium. The author's "experiments differ neither in principle nor in conclusions from those of Dewar," but they "show that the production of liquid hydrogen is neither so difficult nor so costly as might have been expected."

J. C. P.

Electrolytic Preparation of Alkali Periodates. By ERICH MÜLLER (Dresden) (*Zeit. Elektrochem.*, 1901, 7, 509—516).—When a neutral solution of an alkali iodate is electrolysed with platinum electrodes and without a diaphragm, the gas which is at first evolved consists mainly of oxygen, the hydrogen having been employed in reducing iodate to iodide. As the latter accumulates in the solution, it is oxidised at the anode to iodate and the quantity of oxygen evolved also diminishes until finally very little gas is liberated and the solution contains a mixture of iodate and iodide of practically constant composition. In presence of a little potassium chromate practically no reduction occurs; there is also no formation of periodate. In alkaline solutions, however, a considerable yield of periodate is obtained. A series of experiments shows that the most favourable conditions are: low temperature, low current density, and the presence of at least 4 per cent. of sodium or potassium hydroxide. The solution of iodate should be as concentrated as possible and a diaphragm should be present. Sodium periodate separates out as a voluminous powder having approximately the composition $4\text{Na}_3\text{IO}_5 \cdot 5\text{H}_2\text{O}$; the potassium salt obtained is KIO_4 .

Lithium iodide in presence of a little chromate is oxidised to iodate electrolytically by a current of 0.13 amp. per sq. cm. at the anode and 0.59 ampere per sq. cm. at the cathode, the current efficiency being about 94.7 per cent. The iodate could not be further oxidised to periodate, however. T. E.

Determination of the Molecular Weight of Ozone by means of the Balance. By MARIUS OTTO (*Ber.*, 1901, 34, 1118—1119).—The work of Ladenburg (this vol., ii, 232) on this subject has been anticipated by the author (*Abstr.*, 1897, ii, 207).

T. H. P.

Sulphur Trioxide. By RUDOLF SCHENCK (*Annalen*, 1901, 316, 1—17).—The coefficients of expansion of sulphur trioxide determined between the following temperatures 11° , 35.3° , 60.4° , 78.3° , 80.3° , and 100° are 0.0023, 0.0030, 0.0031, 0.0028, and 0.0028 respectively; the critical temperature of the compound is 216° . The existence of polymeric molecules in liquid sulphur trioxide is indicated by a determination of the molecular surface energy after the method introduced by Ramsay and Shields (*Trans.*, 1893, 63, 1089). The coefficient k determined by this process increases as the temperature rises, the values obtained being 1.35 at 17.5° — 35.3° , 1.62 at 35.3° — 60.4° , 1.86 at 60.4° — 78.3° , and 2.30 at 78.3° — 100° . The critical point calculated from the surface tension equation after applying Ramsay and Young's correction is found to be 214.6° . The existence of polymeric molecules in liquid sulphur trioxide supports the view that the asbestos-like form of the solid substance is a polymeric form of the prismatic modification and not a hydrate produced by the action of traces of moisture or sulphuric acid. G. T. M.

Permonosulphuric Acid (Caro's Acid). By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1901, 34, 853—862).—A solution of Caro's acid prepared by acting on potassium persulphate, $\text{K}_2\text{S}_2\text{O}_8$, with sulphuric acid, pouring on to ice and diluting, is completely decom-

posed by the addition of baryta, but can be freed from sulphuric acid by precipitating with barium phosphate. The active oxygen and sulphur in the solution were found to be in the ratio $O:SO_3 = 1:1.156$, and it is therefore supposed that the solution consists mainly of salts derived from permonosulphuric acid, H_2SO_5 [$O:SO_3 = 1:1$], the excess of sulphur being accounted for by the presence in the solution of salts of unchanged perdisulphuric acid, $H_2S_2O_8$ [$O:SO_3 = 1:2$]. These two acids can be estimated separately by making use of the fact that the former acid causes an immediate separation of iodine from an acid solution of potassium iodide, whilst the latter acid acts only very slowly.

A solution of perdisulphuric acid, $H_2S_2O_8$, prepared by the action of dilute sulphuric acid on the barium salt, was found to decompose very slowly into sulphuric acid and permonosulphuric acid; in presence of 40 per cent. sulphuric acid, the conversion was almost complete in seven days, but hydrolysis of the acids to hydrogen peroxide also took place.

The anode acid in the electrolysis of 20 per cent. sulphuric acid was found to contain a relatively large proportion of perdisulphuric acid, which gradually changed into permonosulphuric acid; on electrolysis stronger acids, the change of the perdisulphuric acid into permonosulphuric acid and into hydrogen peroxide was found to have taken place already to a very large extent during the electrolysis.

T. M. L.

Inorganic Acids. By ARTURO MIOLATI and E. MASCETTI (*Gazzetta*, 1901, 31, i, 93—139).—The neutralisation of an acid by a base may be studied by adding successive proportions of base to the solution of the acid and determining the electrical conductivity of the liquid after each addition (compare Miolati, *Abstr.*, 1900, ii, 214). This method has now been applied to the following acids: sulphurous, selenious, selenic, telluric, chromic, arsenic, phosphorous, arsenious, boric, iodic, and periodic, the alkalis employed being sodium and potassium hydroxides and ammonia. The numerical results, which are given in tables and conductivity curves plotted therefrom for each acid, show that a number of the acids examined behave quite analogously to the dibasic acid existing in aqueous solutions of platonic chloride (*loc. cit.*). This anomalous behaviour is exhibited by all those acids which have several replaceable hydrogen atoms possessing different acidic properties. The basicity of such acids varies with the indicator employed in their titration; some of them are monobasic with methyl-orange whilst with phenolphthalein they are dibasic except in the presence of glycerol when certain of them are again monobasic. For the hydrogen metallic salts of some of these acids, the assumption of a double molecule is necessary to explain the change of conductivity on progressive neutralisation of the acids, whilst in some cases it is possible that such double molecules are partially dissociated into single molecules, as is notably the case with the dichromates.

T. H. P.

New Researches on Nitrohydroxylaminic Acid. By ANGELO ANGELI and FRANCESCO ANGELICO (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 249—255. Compare *Abstr.*, 1900, ii, 594).—*Silver nitrohydroxyl-*

amine may be obtained as a voluminous, yellow precipitate resembling silver hyponitrite or lead iodide, by the addition of a silver nitrate solution to a solution of the sodium salt acidified with acetic acid, the mixture being well cooled in a mixture of ice and salt; it is very unstable, and on removal from the cooling mixture rapidly decomposes for the most part in the sense of the equation $\text{NOAg} \cdot \text{NO}_2\text{Ag} = \text{NO}_2\text{Ag} + \text{NO} + \text{Ag}$, the deposited silver having a shining, metallic appearance resembling that of ammonium amalgam.

Nitrohydroxylaminic acid reacts readily with glyoxal or suberaldehyde, yielding hydroxamic acids, which may be separated by means of their insoluble copper salts; in this reaction, the aldehydes behave like alcohols of the form, $\text{CR} \cdot \text{OH}$.

With glyceraldehyde, nitrohydroxylaminic acid readily reacts, but not with dextrose or lactose, a fact which goes to support other evidence indicating that these sugars do not contain aldehyde residues, but have the structure of anhydrides. No action takes place with *o*-nitrobenzaldehyde or salicylaldehyde, helicin, metallic opianates, or pyrrolealdehyde.

The author goes on to discuss the six different ways in which nitrohydroxylaminic acid or its salts decompose, which are as follows: (1) $\text{H}_2\text{N}_2\text{O}_3 = 2\text{NO} + \text{H}_2\text{O}$; (2) $\text{H}_2\text{N}_2\text{O}_3 = \text{HNO}_2 + \text{NOH}$; (3) $\text{H}_2\text{N}_2\text{O}_3 = \text{HNO}_2 + \text{NO} + \text{H}$; (4) $\text{H}_2\text{N}_2\text{O}_3 + \text{H}_2\text{O} = \text{NH}_2 \cdot \text{OH} + \text{HNO}_2 + \text{O}$; (5) $2\text{H}_2\text{N}_2\text{O}_3 = 2\text{HNO}_2 + (\text{NOH})_2$; (6) $2\text{H}_2\text{N}_2\text{O}_3 = 2\text{HNO}_2 + \text{N}_2\text{O} + \text{H}_2\text{O}$.
T. H. P.

Action of Hydrogen Arsenide on Boron Bromide. By ALFRED STOCK (*Ber.*, 1901, 34, 949—956. Compare Besson, *Abstr.*, 1890, 448, 690, and 1891, 1418).—The additive compound $\text{BBr}_3 \cdot \text{AsH}_3$, is obtained when boron bromide is gradually dropped into liquefied hydrogen arsenide contained in a special apparatus and maintained at a temperature of -80° to -100° . It is essential that all moisture and oxygen be previously removed, and the operation is best carried out while a stream of perfectly dry hydrogen is passed through the apparatus. The product is a white, amorphous substance which, when heated, decomposes, but does not melt. It may be obtained in a crystalline form by careful sublimation in a closed vessel. It is insoluble in carbon disulphide, but dissolves in either of its constituents. In contact with air or oxygen, it is readily oxidised, and in most cases is spontaneously inflammable, yielding boric and arsenious oxides, and hydrogen bromide. It is not acted on by oxygen at temperatures below -40° . If the amount of oxygen is carefully regulated and the temperature kept moderately low, the products are boric oxide, hydrogen bromide, and free arsenic, together with arsenic tribromide.

Even at 0° , slow decomposition into its constituents occurs, and this is accelerated if a current of some indifferent gas is employed to remove the hydrogen arsenide as it is formed; a small amount of arsenic is also deposited. When kept for several weeks at the ordinary temperature in a closed vessel protected from light, it is completely decomposed into boron bromide, arsenic, and hydrogen. In contact with water, it is decomposed into boric acid, hydrogen bromide, hydrogen arsenide, and a small amount of free arsenic. Concentrated

sulphuric acid has no apparent action, but concentrated nitric acid produces violent oxidation. Arsenic trichloride reacts with the compound, even at -50° . Ammonia at 10° yields the compound $2\text{BBr}_3, 9\text{NH}_3$. J. J. S.

The Reversible Reaction $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$. By OCTAVE BOUDOUARD (*Bull. Soc. Chim.*, 1901, [iii], 25, 484—489).—A mixture of equal volumes of dry carbon dioxide and hydrogen was heated in a porcelain vessel at 850° and 1100° , and an analysis made at the end of each experiment of the mixture of carbon dioxide, carbon monoxide, hydrogen, and aqueous vapour produced. The results obtained are in fair accordance with Le Chatelier's formula (Abstr., 1900, ii, 199) for the equilibrium of gaseous mixtures, the differences observed being probably due to the condensation of water in the cold portion of the porcelain vessel and, at the higher temperature, to the passage of hydrogen through the walls of the porcelain vessel. The pressure has no influence on the equilibrium, since the numbers of reacting and produced molecules are equal. The reaction is of interest in connection with the manufacture of air and water gas. N. L.

New Researches on the Action of Hydrogen Peroxide on Silver Oxide. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 897—904).—New experiments confirm the author's earlier conclusions (Abstr., 1880, 441; 1899, ii, 149) that the action of hydrogen peroxide on precipitated silver oxide results in the formation of silver peroxide, Ag_2O_2 , part of which decomposes into silver and oxygen, and part into silver oxide and oxygen, whilst a third part combines with the silver oxide so produced and forms an intermediate oxide, Ag_4O_3 . The latter decomposes into silver oxide and oxygen. There are three distinctly recognisable stages in the reaction, but they are not very sharply defined. If the decomposition is rapid and there are sudden local elevations of temperature, the silver peroxide tends to decompose completely into silver and oxygen. C. H. B.

Theory of Technical Processes. By GUIDO BODLÄNDER and P. BREULL (*Zeit. angew. Chem.*, 1901, 14, 381—390, and 405—413).—In the ammonia-soda process, sodium chloride, carbon dioxide, calcium carbonate, and water yield calcium chloride and sodium hydrogen carbonate. The reverse change takes place when solutions of sodium hydrogen carbonate and calcium chloride are mixed. It is shown, however, that the reaction represented by the equation $\text{HCl} + \text{NaHCO}_3 (\text{solid}) = \text{CO}_2 + \text{H}_2\text{O} + \text{NaCl} (\text{solid})$ is accompanied by an absorption of heat amounting to 4020 cal. From the known dissociation of carbonic acid into the ions HCO_3 and H , and their solubility in water and the solubility of sodium hydrogen carbonate in solutions of sodium chloride, the authors have calculated the pressure under which carbon dioxide must be forced into a saturated solution of sodium chloride in order to bring about the reverse change and cause the separation of sodium hydrogen carbonate. This pressure is 3.3 million atmospheres.

From this pressure, the mechanical work required to bring about the reverse change can be calculated; for gram-molecular proportions, it amounts to 3.894×10^8 gr. cm.

By determining the *E.M.F.* of a galvanic element,
 Platinum | $\text{H} + \text{CO}_2$ | $\text{HCl}(0.12N) + \text{saturated NaCl aq.}$ | solution of
 $\text{NaCl} + \text{NaHCO}_3$ (saturated for each) | $\text{H} + \text{CO}_2$ | Platinum,
 the electric energy of the reaction between hydrochloric acid and sodium
 hydrogen carbonate can be estimated; for a pressure of carbon dioxide
 of $\frac{1}{2}$ atmosphere, the electric energy is 38180 Joule = 3.894×10^8 gr.
 cm. Thus, although the chemical reaction is accompanied by an
 absorption of heat, free energy is developed. The temperature coeffi-
 cient of the *E.M.F.*, calculated from the heat change and the electro-
 motive force, is 0.001935, which agrees with the experimental value
 0.00205.

The solubility of sodium hydrogen carbonate in solutions of sodium
 chloride is measured, and agrees very well with the values calculated
 from the law of lowering of solubility (Nernst) for low concentrations
 of sodium chloride. With high concentrations, the experimental
 lowering of solubility is found to be far greater than the calculated
 values.

K. J. P. O.

Spontaneous Crystallisation of the Hydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ from Saturated Solutions of Sodium Sulphate. Limit of the
 Metastable State in these Solutions. By LOUIS C. DE COPPET
 (*Bull. Soc. Chim.*, 1901, [iii], 25, 388—393).—When a saturated solu-
 tion of sodium sulphate is sufficiently cooled, spontaneous crystallisa-
 tion always occurs, even under conditions which preclude the access
 of crystalline nuclei from the atmosphere, and it was shown by the
 author, in 1872, that this takes place between such wide limits of
 temperature as from -13° to $+6^\circ$. More recent observations, details
 of which are given in the paper, show that the formation of the hydrate
 $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ frequently occurs at 8.5° , and has once been observed
 to take place at about 12° . The results are in accord with the con-
 clusions formerly arrived at (*Ann. Chim. Phys.*, 1875, [v], 6, 275), that
 the time required for the spontaneous crystallisation of a supersatur-
 ated solution decreases as the temperature decreases and the concen-
 tration increases. No precise distinction can be drawn between the
 two conditions, termed by Ostwald the metastable state, in which the
 presence of a crystalline nucleus is required for crystallisation, and
 the labile state, in which crystallisation may occur spontaneously.

N. L.

Decomposition of Ammonium Nitrite. By RUDOLF WEG-
 SCHEIDER (*Zeit. physikal. Chem.*, 1901, 36, 543—545).—Owing to the
 fact that the decomposition of ammonium nitrite solutions is accelerated
 by the addition of a salt having a common ion, Angeli and Boeris
 (Abstr., 1893, ii, 155) considered the reaction to be due to the undis-
 sociated molecules, but the author points out that the above facts equally
 support the view that the reaction takes place between the two ions.

L. M. J.

Crystallised Calcium Oxide. By ADOLPHE JOUVE (*Compt. rend.*,
 1901, 132, 1117—1118).—When calcium chloride and carbon are
 heated in an electric furnace under such conditions that the formation
 of calcium carbide is incomplete, a small quantity of calcium oxide is

usually obtained in the form of transparent, acicular prisms of sp. gr. 2.5. C. H. B.

Calcium Sulpho-aluminates and the Decomposition of Maritime Structures made of Portland Cement. By ORAZIO REBUFFAT (*Gazzetta*, 1901, 31, i, 55—57).—The author describes a series of experiments on the action of solutions of magnesium salts and sodium chloride, and of sea-water on calcium sulpho-aluminates, aluminates, and silicates. The results show that the formation of sulpho-aluminates in cement immersed in sea-water is only transitory, and only takes place to a very slight extent, so that the disgregation of the cement cannot be due to this action. Further, sodium chloride has a disintegrating action on the aluminates and on the sulpho-aluminates. T. H. P.

Barium Hydride. By ANTOINE GUNTZ (*Compt. rend.*, 1901, 132, 963—966).—Barium hydride, BaH_2 , a compound whose existence was first indicated by Winkler (*Abstr.*, 1890, 452), is prepared by heating barium amalgam, contained in an iron boat at 1400° in a current of hydrogen; it forms a grey, crystalline mass, having a sp. gr. 4.21 at 0° . The compound melts at 1200° and at 1400° in a current of hydrogen, slowly volatilises without decomposition yielding a green vapour; it is decomposed by water, giving rise to barium hydroxide and hydrogen. When heated in nitrogen, it evolves hydrogen and becomes converted into the corresponding nitride, Ba_3N_2 , the latter compound being contaminated with a large amount of the iron nitride, Fe_3N_2 , produced under these conditions by the interaction of nitrogen and the material of the iron boat. These two nitrides are isomorphous, for the mixture is homogeneous and well crystallised. The amount of the iron compound produced increases with the temperature, and a similar phenomenon is observed when lithium nitride is prepared in an iron or nickel vessel. G. T. M.

Radioactive Lead. By KARL A. HOFMANN and EDUARD STRAUSS (*Ber.*, 1901, 34, 907—913. See this vol., ii, 19, 216).—Continuing their researches on the “pure lead sulphate,” isolated from bröggerite, the authors have separated two “elements,” of which the probable atomic weights are 100.92 and 171.96. The first of these forms a yellow sulphate, and has little influence on the radioactivity of the “lead.” The strong radioactivity of the sulphate of the other “element” is lost when it is converted into the sulphide, but returns when the sulphide is reconverted into the sulphate. The paper concludes with a discussion of the connection between radioactivity and phosphorescence, and between radioactivity and the Becquerel rays. R. H. P.

Alloys made in the Electric Furnace. By LEWIS P. HAMILTON and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1901, 23, 151—155).—The electric furnace employed consisted of two graphite crucibles, placed one within the other, the space between being filled with magnesia; it was provided with two carbon poles, of which the negative was inserted through the side of the crucible at about 3 cm. from the bottom. By means of this apparatus, the authors have prepared a number of alloys containing chiefly the following elements: copper, molybdenum, iron,

chromium, aluminium, tungsten, titanium, columbium, and tantalum. The analysis of each alloy is appended. E. G.

Slow Alteration in Copper Alloys in Contact with Air and Alkali Chlorides. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1901, [vii], 22, 457—460. Compare *ibid.*, 1895, [vii], 4, 552).—Copper alloys, immersed in a sodium chloride solution in contact with air, are slowly disintegrated the copper being converted into the basic chloride, $3\text{CuO} \cdot \text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, corresponding with atacamite; this salt reacts with a further quantity of copper, giving rise to cuprous oxide and sodium cuprous chloride, the latter compound being reconverted into the basic salt by atmospheric oxidation. The other metals of the alloy are also oxidised, and are found partly precipitated and partly in solution. Antique objects now composed of copper oxide were in all probability originally made of some copper alloy, and owe their present composition to the preceding reactions, the oxygen replacing the other constituents of the alloy without altering their contours. G. T. M.

Presence of Acid Sulphate of Copper in Mixtures of Aqueous Solutions of Sulphuric Acid and Copper Sulphate. By CHARLES F. LINDSAY (*Trans. Nov. Scot. Inst. Sci.*, 1900, 10, 205—210).—The amount of alkali required to cause precipitation of copper hydroxide agrees with that necessary for the neutralisation of the sulphuric acid known to be present. There is thus no evidence of the existence of copper hydrogen sulphate in the solution. The specific gravity of the mixture is less than the mean value for the specific gravities of the sulphuric acid and copper sulphate solutions, which agrees with Favre and Valson's observations (*Compt. rend.*, 1873, 77, 907) on mixtures of copper and potassium sulphates. J. McC.

Behaviour of Fluorides of the heavy Metals in Solution. By A. JAEGER (*Zeit. anorg. Chem.*, 1901, 27, 22—40).—Mercuric fluoride is hydrolysed in solution to the extent of about 80 per cent., and this hydrolysis is evidence for the formula H_2F_2 for hydrofluoric acid. Cupric fluoride is hydrolysed to a much less extent. The solubility of mercuric oxide and cupric oxide in hydrofluoric acid is decreased by the addition of potassium fluoride, which proves the non-existence of complex fluorides.

Cadmium fluoride is soluble to the amount of 0.3 gram-mol. in 1000 c.c. of water, and slightly more soluble in hydrofluoric acid.

Lead fluoride is very slightly soluble in dilute hydrofluoric acid, but insoluble in stronger acid. Lead hydroxide decomposes the alkali haloids until equilibrium is obtained with the free alkali, depending on the solubility of the lead haloids; it also appears to form complex compounds with the lead haloids. E. C. R.

Mercury Iodoantimonide. By ALBERT GRANGER (*Compt. rend.*, 1901, 132, 1115—1116).—Mercury iodoantimonide, $\text{Hg}_3\text{Sb}_4 \cdot 2\text{HgI}_2$, is obtained in grey, lustrous, brittle, prismatic crystals by heating mercury at 300° in sealed tubes with a slight excess of antimony triiodide, and removing mercuric iodide from the product by treatment with a strong solution of sodium sulphite. When heated, the iodoantimonide is decomposed into mercuric iodide, mercury, and anti-

mony; it is readily attacked by chlorine, bromine, nitric acid, and hot sulphuric acid, but not by hydrochloric acid. It is also decomposed by a warm solution of ferric chloride, and is reduced by zinc and dilute sulphuric acid, especially on heating. C. H. B.

Praseodymium. By CARL VON SCHÉELE (*Zeit. anorg. Chem.*, 1901, 27, 53—57).—A criticism of Muthmann's work (*Abstr.*, 1900, ii, 18). A spectroscopic examination of the praseodymium oxide employed in the author's previous work shows that it is free from lanthanum.

E. C. R.

Zirconium Earth in Euxenite from Brevig. By KARL A. HOFMANN and W. PRANDTL (*Ber.*, 1901, 34, 1064—1069).—In extracting the small quantities of lead from euxenite from Brevig (*Abstr.*, 1900, ii, 216; this vol., ii, 19), a zirconium earth was found in the residue of sulphates, the properties of which indicated the presence of the oxide of an unknown metal. The separation of the latter compound from the zirconia is described.

The oxide, which the authors term provisionally 'euxenium earth,' is white, and, after ignition, is only sparingly soluble in acids. When fused with sodium hydrogen sulphate, treated with sulphuric acid, and evaporated to dryness, a residue is obtained which yields a colourless solution. On the addition of an alkali to the solution, a white, flocculent precipitate is produced which is insoluble in excess. With hydrogen peroxide, a white precipitate is gradually formed. Oxalic acid yields no precipitate. If a solution of the chloride is treated with zinc and hydrochloric acid, no coloration is produced. When tannic acid is added to a faintly acid solution, a yellowish-brown precipitate is obtained. Potassium ferrocyanide gives, after a few minutes, a brown precipitate. The oxide differs from that of zirconium in yielding a precipitate with excess of ammonium carbonate and in giving no coloration with turmeric. Determinations of the equivalent by means of the sulphate gave 44·4—44·5, whence the atomic weight calculated for a quadrivalent element would be 177·6—178.

In addition to the 'euxenium earth,' small quantities of another unknown substance are present, which furnishes a yellow chloride; its solutions yield a brownish-yellow precipitate with potassium ferrocyanide, and are reduced by zinc and hydrochloric acid with production of a greenish-brown coloration; it is perhaps related to tantalum, but possesses a pronounced basic character.

Analyses of specimens of euxenite (I) from Arendal and (II) from Brevig gave the following results:

| | Loss on Ignition. | SiO ₂ . | TiO ₂ . | Nb ₂ O ₅ . | PbO. | Ytterbium and Cerium oxides. |
|-----|---------------------------------|--------------------|----------------------------------|----------------------------------|------|---------------------------------|
| I. | 1·91 | 0·19 | 17·35 | 33·56 | 1·07 | 35·34 |
| II. | 2·06 | 20·94 | 20·72 | 10·79 | 0·43 | 21·90 |
| | U ₃ O ₈ . | ZnO. | Fe ₂ O ₃ . | Al ₂ O ₃ . | CaO. | Total. |
| I. | 4·37 | 1·30 | 1·58 | 3·71 | — | 100·28 |
| II. | 2·93 | 1·97 | 9·27 | 9·22 | 0·67 | 100·90 |

The constituent of the euxenite from Brevig calculated as zirconia

contained 'euxenium earth' to the extent of about one-half of its weight. E. G.

Heat of Rapid Combustion of Aluminium. By MARCELLIN P. F. BERTHELOT (*Ann. Chim. Phys.*, 1901, 22, [vii], 479—482).—The heat of combustion of aluminium has hitherto been determined indirectly, as it is not readily burnt in a calorimeter even with compressed oxygen in the presence of camphor. A mixture of aluminium, aluminium carbide, camphor, and gun-cotton can, however, be completely oxidised, and the heat of formation of aluminium oxide deduced from this experiment is 380.2 Cal., that of the hydrated substance being 393.0 Cal. G. T. M.

Aluminium Alloys: Combination of Aluminium and Tungsten. By LÉON GUILLET (*Compt. rend.*, 1901, 132, 1112—1115).—An intimate mixture of tungstic anhydride with finely divided aluminium was placed in a crucible brasqued with magnesium oxide, and ignited by means of a mixture of barium peroxide and aluminium, when a somewhat violent combustion occurs. In this way, crystallised alloys of tungsten and aluminium are obtained, the composition of which depends on that of the original mixture. If the latter is between that required to produce theoretically AlW_{10} and Al_5W respectively, the product is AlW_2 ; if between AlW and $Al_{10}W$, the product is Al_4W ; if between Al_3W and AlW_5 , the product is Al_3W .

In analysing the alloys AlW_2 and Al_3W , sodium peroxide was found to be the best reagent for attacking them, as they are but little soluble in aqua regia, which, however, readily dissolves the alloy Al_4W .

C. H. B.

Action of Heat on Potassium Permanganate. By GEORGE RUDORF (*Zeit. anorg. Chem.*, 1901, 27, 58—61).—When potassium permanganate is heated over a bunsen burner the decomposition which takes place may be represented by the equation $10KMnO_4 = 3K_2MnO_4 + 7MnO_2 + 6O_2 + 2K_2O$, or there are formed 12.14 per cent. oxygen, 37.42 per cent. potassium manganate and 38.51 per cent. manganese dioxide. E. C. R.

Rate of Dissolution of Iron in Hydrochloric Acid. By JAMES T. CONROY (*J. Soc. Chem. Ind.*, 1901, 20, 316—320).—When iron dissolves in hydrochloric acid, the rate of dissolution is initially slow during the "period of induction" (Spring and Van Aubel, *Abstr.*, 1887, 1074), then attains a maximum value, and afterwards diminishes; in the following statements, the term "rate of action" refers to the *maximum* rate of action, this being determined by measuring the maximum rate at which hydrogen is evolved from thin plates of iron of equal area immersed in acid of different concentrations and at different temperatures. Curves are given showing the influence of these conditions on the rate of dissolution; as the concentration increases the rate of action increases in geometrical progression over "a considerable range," in such manner that the rate of dissolution is doubled for each increase of 30 grams of hydrogen chloride per litre. A similar law connects the rate of dissolution and temperature, the former being doubled for each 10° rise of the latter for concentrations between 25 and 216 grams of hydrogen chloride per litre.

When traces of arsenic are present in the acid used, the rate of dissolution is considerably diminished; when present in larger quantities, the iron becomes completely covered with a film of arsenic, and action almost completely ceases, even in the case of the more concentrated acids.

W. A. D.

Oxides of Cobalt. By ERWIN HÜTTNER (*Zeit. anorg. Chem.*, 1901, 27, 81—124).—Cobalt sulphate when oxidised by means of (a) potassium persulphate in alkaline solution, (b) ammonium persulphate in acid solution, (c) ammonium persulphate in alkaline solution, or (d) chlorine gas, yields only the cobaltic oxide Co_2O_3 . The state of hydration of the precipitated oxide depends on conditions which have not been ascertained and the various products obtained were: $\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$; $2\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; and $3\text{Co}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

When oxidised by sodium hypochlorite, a product is obtained which contains more oxygen than Co_2O_3 and corresponds approximately with $\text{Co}_{12}\text{O}_{19}$. An alkaline solution of potassium cobalt sulphate, when oxidised with excess of iodine, gives a black precipitate of CoO_2 . If less iodine be used, a less highly oxidised compound is obtained. The electrolysis of a solution containing cobalt sulphate and a large amount of potassium chloride yields the same oxide, namely, Co_2O_3 , as oxidation by means of chlorine. It is therefore only by the direct application of hypochlorite that a higher state of oxidation than that represented by Co_2O_3 is reached.

Coehn and Salomon (*Abstr.*, 1899, ii, 127) have suggested that a separation of cobalt and nickel may be carried out by electrolytically depositing cobalt superoxide at the anode. The author finds that on electrolysing a neutral solution of cobalt sulphate, a precipitate is formed at the anode but is quickly redissolved (by the acid liberated). To prevent this re-solution the whole was kept continually neutral by the gradual addition of sodium carbonate, and the precipitate so formed was found to be Co_2O_3 . Coehn's surmise of the production of the superoxide is consequently not confirmed.

J. McC.

Some Cobalt Reactions. By EDUARD DONATH (*Zeit. anal. Chem.*, 1901, 40, 137—141).—The majority of text-books ignore the solubility of cobaltous hydroxide in concentrated alkali hydroxide solutions (see, however, Reichel, *Abstr.*, 1881, 194; also 1893, ii, 468). On adding either a soluble or insoluble cobalt salt, or any cobalt ore after roasting, to a hot 80 per cent. solution of potassium hydroxide, a blue solution is obtained. Cupric oxide gives a similar blue solution under the same conditions. The two can be distinguished as follows: addition of an alkali tartrate somewhat deepens the colour of the copper solution but nearly decolorises that of cobalt, leaving very strong solutions slightly reddish; addition of potassium cyanide decolorises the copper solution completely, but leaves the cobalt solution yellowish, and this yellow solution, when in contact with air, rapidly acquires a deep brown colour. Whilst with aqueous alkali solutions the cobalt compound added is never wholly redissolved, a mixture containing glycerol gives no precipitate with a cobalt salt, either in the cold or on boiling. The blue solution produced in this case becomes green by absorption of oxygen or by addition of hydrogen

peroxide. The author suggests that the blue solution contains potassium cobaltite, Co(OK)_2 , in a non-ionised condition. M. J. S.

Uranium Nitrate and Sulphate. By WILLIAM OECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1901, 3, 222—226. Compare this vol., ii, 104, 105, 164, 165).—Uranium nitrate crystals lose H_2O at 100° , the second mol. between 100° and 115° , and the third between 115° and 130° . On heating at 255° , they decompose, giving nitrogen peroxide and oxygen and leave a solid residue of uranium sesquioxide.

Solutions of uranium nitrate in hydrobromic acid solution (sp. gr. 1.21) have the following sp. gr. :

| Temp. | 16.8°. | 15.2°. | 17.4°. | 14.7°. | 15.3°. |
|--------------------------------------|--------|--------|--------|--------|--------|
| Percentage of dissolved salt | 1 | 2 | 3 | 4 | 5 |
| Sp. gr. ($\text{H}_2\text{O} = 1$) | 1.2122 | 1.2168 | 1.2198 | 1.2250 | 1.2305 |

The sp. heat of a 10 per cent. solution is 0.946. An 8 per cent. solution has $n. 1.338$, a 10 per cent. solution $n. 1.348$, and a 12 per cent. solution $n. 1.364$.

Uranium sulphate loses 1.5 H_2O at 100° and at 110 — 115° another 0.5 mol. is expelled. At 175° , the third mol. is driven off. At a dull red heat, the salt is decomposed and leaves a residue which consists of a mixture of the oxides U_2O_3 and U_3O_4 . Heated rapidly it gives a residue of the black oxide, U_4O_5 . J. McC.

Studies on Solutions of Stannous Salts. II. The Oxidation of Solutions of Stannous Chloride by means of Free Oxygen. By STEWART W. YOUNG (*J. Amer. Chem. Soc.*, 1901, 23, 119—147. Compare this vol., ii, 318).—A solution of stannous chloride was thoroughly shaken with pure oxygen in a flask by means of a specially devised apparatus; the decrease in the volume of the oxygen for definite periods of time was measured by means of a gas burette, the temperature being kept constant. The residual stannous chloride was titrated with solution of potassium dichromate.

It was found that the velocity constant increases considerably during the first thirty or forty minutes, but that if semi-normal hydrochloric acid is added to the solution this acceleration is much less marked; the values obtained vary greatly in different series of experiments, but for a given series in which the stannous chloride is of the same strength throughout, the increase is approximately proportional to the concentration of the hydrochloric acid. These facts find their simplest explanation in the supposition that the hydrochloric acid produced by the reaction tends to diminish the proportion of stannous chloride hydrolysed.

The rate of oxidation increases to a certain extent with the age of the solution; solutions kept for some time in previously exhausted sealed tubes, exhibited a rate of oxidation more than double that of a solution prepared in the flask immediately before the experiment. If a tube of the solution was opened and left for about 20 minutes in the air, different portions of the solution gave results in approximate agreement; but if the tube was not opened until immediately before an experiment, and the first portion introduced at once into the apparatus, this first portion invariably yielded higher results than succeed-

ing portions, whilst the results of the latter agreed fairly well with one another.

Experiments carried out in order to determine if re-exhaustion of the tube would remove the agent which caused the depression in the rate of oxidation showed that it had no apparent effect; light also has no appreciable influence on the reaction.

The reaction between stannous chloride and oxygen hence appears to be extremely sensitive to small quantities of substances with which the reagents may come in contact in the ordinary methods of manipulation; the influence of a number of such substances was therefore investigated. It was found that india-rubber, sulphur, hydrogen sulphide, salts of iron and copper, and alcohol cause an acceleration in the rate of oxidation, whilst salts of manganese and chromium, tobacco smoke and extract, brucine, morphine, nicotine, mannitol, aniline and potassium cyanide produce a retardation; pyridine and phenol do not exert any considerable influence. E. G.

Metathoric Acid and Metathorium Oxychloride. By HENRY P. STEVENS (*Zeit. anorg. Chem.*, 1901, 27, 41–62).—A repetition of Locke's work (*Abstr.*, 1895, ii, 49) shows that the formula of metathorium oxide is not Th_3O_5 but ThO_2 ; that is, it has the same composition as ordinary thorium oxide.

Metathorium oxide, prepared by heating the oxalate, when treated with dry hydrogen chloride, is converted into oxychloride which contains chlorine varying from 0.61 to 10 per cent., according to the amount of water contained in the metathorium oxide. Metathorium oxide, like silicic acid, retains water persistently, but when it is dried by heating in a current of dry air it is no longer acted on by hydrogen chloride. The reaction which takes place between the oxide containing water and chlorine corresponds with the formula $\text{ThO}_2 \cdot x\text{ThCl}_4$ for the oxychloride.

Metathorium oxychloride is a white, hygroscopic powder which dissolves in water to a clear solution when it contains 9 to 10 per cent. of chlorine; the preparations with less chlorine yield a more or less opalescent solution. It has an acid reaction, is insoluble in absolute alcohol, dissolves in alcohol containing a small quantity of water, behaves towards reagents in a similar manner to metastannic chloride, and is precipitated by many normal salts and by excess of acid, this precipitation taking place more easily the less chlorine it contains. When treated with silver nitrate, it does not give a precipitate of silver chloride.

Metathorium hydroxide, or metathoric acid, prepared by precipitating the oxychloride with ammonia, unlike thoracic acid, does not absorb carbon dioxide from the air, and is less basic. It is gradually converted into thoracic acid when allowed to remain in contact with water, and dissolves in mineral acids if an excess of acid is carefully avoided. When prepared from a metaoxychloride rich in chlorine, it requires more acid for solution than when prepared from a compound poor in chlorine, and a solution of metaoxychloride requires more acid to precipitate it as the percentage of chlorine increases. The author

points out the similarity between metathoric acid and metastannic acid.
E. C. R.

Rhodium Alums. The Separation of Rhodium from Iridium. By AUGUSTO PICCINI and L. MARINO (*Zeit. anorg. Chem.*, 1901, 27, 62—71).—Rhodium alums are obtained by mixing a sulphuric acid solution of yellow rhodium sesquioxide with the alkali sulphate, and allowing the mixture to crystallise. The conditions under which these alums are formed are, that only about two-thirds of the theoretical quantity of alkali sulphate and an excess of sulphuric acid are present, and that the solutions are not heated at too high a temperature.

Rhodium cæsium alum, $\text{Rh}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, is sparingly soluble in cold water, much more so in warm water, melts at $110\text{--}111^\circ$, and when dried at $180\text{--}250^\circ$ turns brown, with a loss of a small quantity of sulphuric acid, but is still completely soluble in water. The corresponding *rubidium*, *potassium*, *ammonium*, and *thallium* salts are described. These salts all form characteristic, transparent, regular crystals of a more or less deep yellow colour, and are more soluble than the ordinary alums.

Rhodium is easily separated from iridium by adding to a solution of the sulphates a solution of cæsium sulphate; the rhodium cæsium sulphate is, after recrystallisation, quite free from iridium. By subjecting the solution of the alum to electrolysis, the rhodium is easily obtained in a pure state, and the cæsium sulphate which remains in solution can be employed for another precipitation of the alum.

E. C. R.

Mineralogical Chemistry.

Crystallised Stannite from Bolivia. By LEONARD J. SPENCER with analyses by GEORGE T. PRIOR (*Min. Mag.*, 1901, 13, 54—65).—At various times, no less than four types of symmetry have been ascribed to the rare and indistinct crystals of stannite, the one at present usually accepted being tetrahedral-cubic. The distinct crystals from Oruro, Bolivia, now described, are associated with mispickel, andorite, augelite, chalcostibite, jamesonite, pyrites, &c.; they are scalenohedral-tetragonal, with $(001):(101)=44^{\circ}30'$. Usually three crystals are twinned together on (101) and (011) , giving rise to pseudo-tetrahedral-cubic groups. Twinning also takes place on (111) , as in cubic crystals. The colour is iron-black, with a bright metallic to sub-adamantine lustre; streak, black. The mean of two analyses, which are the first that have been made on crystallised material, is given under I; under II is given the composition of the stannite after deducting 8.58 per cent. of admixed andorite. This agrees with the formula, $\text{Cu}_2\text{FeSnS}_4$, usually given for the mineral.

| | Cu. | Fe. | Sn. | Sb. | Pb. | Ag. | S. | Total. | Sp. gr |
|-----|-------|-------|-------|-------|------|------|-------|--------|--------|
| I. | 28.56 | 10.93 | 25.21 | 3.71 | 2.06 | 0.88 | 27.83 | 99.18 | — |
| II. | 31.52 | 12.06 | 27.83 | 28.59 | — | — | — | 100.00 | 4.45 |

In the symmetry, peculiar twin-laws, and angles, stannite, $(\text{CuFeS}_2, \text{CuSnS}_2)$, is crystallographically almost identical with copper pyrites (CuFeS_2) . Indistinct crystals of stannite are described from two other Bolivian localities and from Cornwall. L. J. S.

Melonite. By ARTHUR DIESELDORFF (*Centr. Min.*, 1901, 168—170).—The following is the mean of three new analyses by P. Georgi of selected melonite from Worturpa, South Australia (compare Abstr., 1900, ii, 283, 664). Sp. gr. 7·36. There is about 3 per cent. of selenium.

| Te(Se). | Ni. | Co. | Fe. | Al. | Bi. | Ag. | Au. | Ca. | Total. |
|---------|-------|------|------|------|------|------|------|------|--------|
| 80·17 | 16·73 | 0·75 | 1·33 | 0·29 | 0·04 | 0·08 | 0·32 | 0·12 | 99·83 |

These results agree with the formula NiTe_2 , in which the nickel is partly replaced by iron and cobalt, and the tellurium by selenium.

This formula, NiTe_2 , in place of the old formula Ni_2Te_3 , has already been given by Hillebrand for Californian melonite (Abstr., 1900, ii, 22). The mineral is sometimes found as six-sided plates with a perfect cleavage parallel to the plane of the plate; for this reason it may belong to the sylvanite group. L. J. S.

Tellurides of Gold and Silver from Western Australia. By P. KRUSCH (*Centr. Min.*, 1901, 199—202).—The tellurides of the Coolgardie gold-field occur as veins in a schistose amphibolite; the upper, oxidised portions of the veins carry free gold. Sylvanite (compare Abstr., 1897, ii, 503), of a silver-white colour and with a perfect cleavage in one direction, gave analysis I, by Wölbling, agreeing with formula $(\text{Au}, \text{Ag})\text{Te}_2$. Calaverite (compare Abstr., 1898, ii, 385), of a pale bronze-yellow colour with a yellowish-grey streak and conchoidal fracture, gave II; formula $(\text{Au}, \text{Ag})\text{Te}_2$. Petzite, steel-grey to iron-black with conchoidal fracture, gave III; formula $(\text{Ag}, \text{Au})_2\text{Te}$; this occurs very abundantly. Another mineral, differing somewhat from petzite in appearance, is almost blue-grey and has indications of a cleavage: this gave the results under IV (contains also Sb 0·12, Zn 0·04); formula $(\text{Ag}, \text{Au})_5\text{Te}_3$.

| | Au. | Ag. | Cu. | Fe. | Ni. | Te. | Se. | S. | Gangue. | Total. |
|------|-------|-------|------|------|------|-------|------|------|---------|--------|
| I. | 28·55 | 9·76 | 0·32 | 0·06 | 0·10 | 60·83 | 0·20 | 0·09 | 0·05 | 99·96 |
| II. | 37·54 | 2·06 | 0·29 | 0·09 | 0·07 | 58·63 | 1·13 | 0·10 | 0·23 | 100·14 |
| III. | 24·33 | 40·70 | 0·10 | 0·07 | 0·08 | 32·60 | 1·45 | 0·26 | 0·12 | 99·71 |
| IV. | 15·06 | 45·95 | 1·16 | 0·08 | 0·06 | 36·90 | — | 0·45 | 0·22 | 100·04 |

Associated with these tellurides, and somewhat resembling them in appearance, is a copper ore which gave the following results on analysis; the atomic ratios $\text{Cu}(\text{ZnFe}) : \text{As}(\text{Sb}) : \text{S} = 78 : 27 : 90$, approach those of enargite $(\text{Cu}_3\text{AsS}_4)$.

| Cu. | Ag. | Au. | Fe. | Zn. | Ni. | Pb. | S. | As. | Sb. | Te. | Gangue. |
|-------|------|------|------|------|------|------|-------|-------|------|------|---------|
| 41·69 | 0·22 | 0·12 | 4·76 | 2·68 | 0·15 | 0·10 | 28·43 | 16·87 | 4·30 | 0·05 | 0·26 |

L. J. S.

Quartz and Gelatinous Silicic Acid from the Simplon Tunnel. By GIORGIO SPEZIA (*Zeit. Kryst. Min.*, 1901, 34, 289—290; from *Atti R. Accad. Sci. Torino*, 1899, 34, 705—713).—A crevice 10 cm. wide in the gneiss of the Simplon Tunnel is filled with a gelatinous

substance resembling vaselin in appearance. Embedded in this are numerous extremely minute quartz crystals, small rhombohedra of ankerite, and a few crystals of pyrites and scales of mica. The ankerite has the composition, CaCO_3 , 59.55; MgCO_3 , 20.90; FeCO_3 , 19.55 = 100.00. The gelatinous substance loses water on exposure to the air, and about 48 per cent. at 100° ; at a red heat there is a further loss of 4.4 per cent. The calcined material contains 93 per cent. of silica. The substance is only slightly soluble in warm potassium hydroxide, and the insoluble portion is not affected by hydrochloric acid or by hot concentrated sulphuric acid. This residue has the composition, SiO_2 , 57.53; Al_2O_3 , with a trace of Fe_2O_3 , 38.02; CaO , MgO , 4.45 = 100.00. It is, therefore concluded that the substance is a mechanical mixture of silicic acid and aluminium hydroxide, both in a colloidal condition. The resistance of the aluminium hydroxide to acids and alkalis is explained by it having remained for a long period in contact with water. Gelatinous silicic acid which has been in contact with water for several years is also not immediately dissolved by potassium hydroxide; and that now described from the Simplon Tunnel probably represents a stage in the passage to quartz.

L. J. S.

Analysis of Limonite from Monte Valerio. By E. MANASSE (*Proc. verb. Soc. Toscana Sci. Nat.*, 1899, 12, 21—22).—Analysis of limonite gave:

| H_2O . | SiO_2 . | SO_3 . | Al_2O_3 . | Fe_2O_3 . | Total. | Sp. gr. |
|------------------------|------------------|-----------------|---------------------------|---------------------------|--------|---------|
| 13.28 | 1.24 | 1.32 | 1.91 | 81.15 | 98.90 | 3.32 |

also traces of CaO , P_2O_5 , and As_2O_5 .

L. J. S.

Marshite, Miersite and Iodyrite. By LEONARD J. SPENCER (*Min. Mag.*, 1901, 13, 38—53).—A description is given of crystals of marshite, miersite and iodyrite from Broken Hill, New South Wales. Marshite, CuI (Abstr., 1895, ii, 504), and the new mineral miersite, $(\text{Ag}, \text{Cu})\text{I}$, are tetrahedral-cubic with crystallographic characters identical with those of zinc-blende. The crystals of iodyrite are of two types: (a) hexagonal plates or prisms, (b) pseudo-cubic crystals of tetrahedral habit, like marshite and miersite, but really consisting of four simple rhombohedral crystals twinned together; the former have been formed below 146° (assuming atmospheric pressure), and the latter at a temperature higher than this. When miersite is fused on a microscope slide, two distinct changes in state are to be observed during the cooling, and by comparing these changes with those shown by copper iodide and silver iodide in known proportions, the composition of miersite is deduced as probably being $4\text{AgI}, \text{CuI}$. This appears to be a molecular compound, which on one hand mixes isomorphously with marshite, and on the other forms intimate and regular intergrowths with iodyrite of type (b). The same relation exists between miersite and iodyrite as between zinc-blende and wurtzite, and so far as crystallographic characters are concerned these form a perfect example of an isomorphous group; but apparently the only chemical relation between zinc sulphide and silver iodide is that their simplest conceivable molecules contain two atoms.

L. J. S.

Relation of Conchite to Aragonite. By REINHARD BRAUNS (*Centr. Min.*, 1901, 134—135).—The characters given for conchite (this vol., ii, 168) are sufficiently close, considering the unsatisfactory nature of the material available for examination, to those of aragonite to point to their identity. L. J. S.

Manganese Minerals from Hautes-Pyrénées. By ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1900, 23, 251—255).—The schistose limestones of the mountain of Serre d'Azet are impregnated with rhodonite, friedelite, rhodochrosite, alabandite, hübnerite, tephroite and various manganese oxides. The supposed new minerals viellaaurite ($5\text{MnCO}_3 \cdot 2\text{Mn}_2\text{SiO}_4$) and torrensite ($\text{MnCO}_3 \cdot \text{MnSiO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$) from this locality (*Abstr.*, 1899, ii, 761) are shown on a microscopical examination to be really rocks. The former consists of a mixture of grains of rhodochrosite (MnCO_3) and tephroite (Mn_2SiO_4) with a little alabandite, and the latter of rhodochrosite and rhodonite (MnSiO_3) in part altered by hydration. L. J. S.

Sphærocobaltite from Libiola, Italy. By A. A. FERRO (*Zeit. Kryst. Min.*, 1901, 34, 302; from *Atti Soc. Ligustica, Sci. Nat., etc., Genova*, 1899, 10, 264—268).—A specimen of quartz and chalcocite from Libiola, near Casarze in Liguria, is coated with a thin crust consisting of a mixture of chessylite, malachite and a cherry-red mineral shown by the following analysis to be sphærocobaltite. At 110° , there is a loss of 0.43 per cent. of water.

| CoO. | H ₂ O(260°). | CuO. | FeO. | CaO. | CO ₂ . | Total. |
|-------|-------------------------|------|------|------|-------------------|--------|
| 59.68 | 0.25 | 2.87 | 0.90 | 0.18 | [36.12] | 100.00 |

The water and copper are present as chessylite.

L. J. S.

Hussakite, a New Mineral allied to Xenotime. By E. H. KRAUS and J. REITINGER (*Zeit. Kryst. Min.*, 1901, 34, 268—277).—The xenotime of Dattas near Diamantina in Brazil, analysed by Gorceix in 1886, is shown by a new analysis (I) not to be an orthophosphate of rare earths but a sulphato-phosphate with the formula $3\text{R}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot \text{SO}_3$. The new name hussakite is given because of this difference in composition. It is found in sands as long prismatic crystals with a very good prism cleavage; these are yellow to brown and transparent and quite fresh. The angles are the same as for ordinary xenotime. Sp. gr. 4.587. Optical determinations are given.

| | SO ₃ . | P ₂ O ₅ . | Y ₂ O ₃ . | Er ₂ O ₃ . | Gd ₂ O ₃ . | Fe ₂ O ₃ . | Al ₂ O ₃ . | CaO. | MgO. | Total. |
|-----|-------------------|---------------------------------|---------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|------|------|--------|
| I. | 6.13 | 33.51 | 43.43 | 14.82 | 1.99 | 0.20 | traces | | | 100.08 |
| II. | 2.68 | 27.37 | 45.86 | 13.67 | 0.42 | 4.54 | 1.16 | 2.56 | 0.45 | 99.70 |

Analysis II (contains also SiO_2 0.62, H_2O 0.37) is of pyramidal crystals of cloudy, opaque xenotime from sands at Bandeira de Mello, Bahia, Brazil. This appears to be intermediate between xenotime and hussakite. Sulphur trioxide was also found in slightly altered xenotime from Hitterö, but not in the much altered xenotime of other Norwegian localities. It thus appears that hussakite is liable to alteration, the sulphur trioxide being extracted, and that ordinary

xenotime containing no sulphur trioxide is really a pseudomorph after hussakite. This is supported by the fact that the sulphur trioxide is easily extracted from powdered hussakite by digestion with hot soda solution.

L. J. S.

A British Occurrence of Mirabilite. By CHARLES O. TRECHMANN (*Min. Mag.*, 1901, 13, 73—74).—Colourless, transparent mirabilite has been found as small, irregular masses in gypsum-rock at Kirkby Thore in Westmoreland. The following analytical results agree closely with the usual formula, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$:

| Na. | SO_4 . | H_2O . | Total. |
|-------|-----------------|------------------------|--------|
| 13.85 | 30.19 | 55.28 | 99.32 |

L. J. S.

Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XXI. Formation of Kainite at 25°. By JACOBUS H. VAN'T HOFF and WILHELM MEYERHOFFER (*Sitzungsber. Akad. Wiss. Berlin*, 1901, 420—427).—The indication previously obtained (this vol., ii, 249) of the formation of kainite ($\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$) at 25° has been confirmed. The conditions of its formation have been studied, and the results are treated graphically, as in earlier papers.

J. C. P.

Analysis of a Bröggerite. By KARL A. HOFMANN and W. HEIDEPRIEM (*Ber.*, 1901, 34, 914—915).—The specimen of bröggerite from Raade near Moss in Norway from which radioactive lead was obtained (see this vol., ii, 216) had a hardness 5.5 and a sp. gr. 9.06 at 15°. Analysis gave:

| UO_2 . | UO_3 . | ThO_2 . | Yttria earths. | Fe_2O_3 . | Bi_2O_3 . | PbO . |
|-----------------|-----------------|------------------|-------------------|---------------------------|---------------------------|----------------|
| 50.00 | 27.83 | 4.96 | 4.56 | 0.46 | 0.35 | 9.21 |

R. H. P.

Forsterite from Latium: Dioptase from Siberia. By FERRUCCIO ZAMBONINI (*Zeit. Kryst. Min.*, 1901, 34, 228—229).—Analysis of transparent, almost colourless crystals of forsterite from the Albanian Mountains, gave:

| SiO_2 . | MgO . | FeO . | CaO . | $(\text{Na}, \text{K})_2\text{O}$. | Total. |
|------------------|----------------|----------------|----------------|-------------------------------------|--------|
| 42.06 | 55.93 | 1.15 | 0.28 | 0.21 | 99.63 |

The following analysis of small crystals of dioptase from Altyn-Tübe, in the Kirghese Steppes, agrees with the usual formula H_2CuSiO_4 .

| SiO_2 . | CuO . | Fe_2O_3 . | H_2O . | Total. |
|------------------|----------------|---------------------------|------------------------|--------|
| 38.25 | 50.18 | 0.13 | 11.39 | 99.95 |

L. J. S.

Analysis of a Zeolite. By G. ONGARO (*Zeit. Kryst. Min.*, 1901, 34, 310; from *Rivista di Min., &c.*, 1899—1900, 23, 35—36).—The mineral analysed occurs as radial red masses mixed with calcite in the augite-porphry of the Valle dei Zuccanti, and is known as "red natrolite." The following composition of the pure transparent crystals approaches that of stilbite:

| SiO ₂ . | Al ₂ O ₃ . | CaO. | Na ₂ O. | H ₂ O. | Total. |
|--------------------|----------------------------------|------|--------------------|-------------------|--------|
| 58·76 | 17·13 | 9·37 | 0·23 | 14·47 | 99·96 |
| L. J. S. | | | | | |

Analysis of White Microcline from the Ilmen Mountains. By J. SIOMA (*Zeit. Kryst. Min.*, 1901, 34, 278—279).—White microcline is an important constituent of the eläolite-syenite of the Ilmen Mountains, Urals. The cleavage angle, 010 : 001, varies between 89°53' and 90°30'. Extinction on 001, -1°30'; on 010, -7°30'. Sp. gr. 2·592. In composition it resembles the cryptoperthite of the Norwegian eläolite-syenite.

| SiO ₂ . | Al ₂ O ₃ (trace Fe ₂ O ₃). | CaO. | MgO. | K ₂ O. | Na ₂ O. | H ₂ O. | Total. |
|--------------------|--|------|------|-------------------|--------------------|-------------------|--------|
| 65·48 | 21·12 | 1·44 | 0·17 | 6·56 | 5·25 | 0·18 | 100·20 |
| L. J. S. | | | | | | | |

Müllerite, Melite, and Schrötterite. By FERRUCCIO ZAMBONINI (*Zeit. Kryst. Min.*, 1901, 34, 225—227. Compare Abstr., 1900, ii, 149).—Müllerite is identical with a mineral [chloropal] from Starbo, Sweden, analysed by Weibull in 1881. The author's first analysis of schrötterite from Saalfeld, Thuringia, was made on material intimately intergrown with melite. The following new analysis gives the formula 7Al₂O₃, 3SiO₂, 36H₂O.

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | H ₂ O. | Total. |
|--------------------|----------------------------------|----------------------------------|------|-------------------|--------|
| 11·73 | 45·78 | 0·31 | 0·24 | 41·67 | 99·73 |

The formula of melite is now given as 2(Al, Fe)₂O₃, SiO₂, 8H₂O.

L. J. S.

Termierite and Lassallite, Two New Silicates. By GEORGES FRIEDEL (*Bull. Soc. franç. Min.*, 1901, 24, 6—14).—The antimony vein of Miramont, in the concession of Souliac on the borders of Cantal and Haute-Loire, contains stibnite, barytes, and the three following substances : I, a white, finely crystalline powder with the optical and chemical (anal. I) characters of kaolinite. II, resembles clay in appearance, and receives the new name *termierite*. Under the microscope it is birefringent. In dry air it loses water and becomes opaque; at 110° it still contains 6·8 per cent. of water; when immersed in water it absorbs 72·4 per cent., increasing in volume and becoming translucent. Analysis II is of the calcined material; the formula is given as 6SiO₂, Al₂O₃ + 18H₂O. III has the appearance of felted asbestos, and receives the new name *lassallite*. Under the microscope it is seen to consist of fine birefringent fibres. In the natural state it contains about 30 per cent. of water, and at 100° still contains 14·22 per cent. When immersed in water it swells up and becomes viscous. Analysis III is of the calcined material. Formula, 12SiO₂, 2Al₂O₃, 3MgO + 8H₂O.

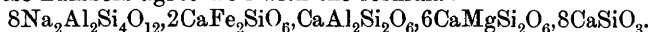
| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | MgO. | K ₂ O. | H ₂ O. | Total. |
|------|--------------------|----------------------------------|----------------------------------|------|-------|-------------------|-------------------|--------|
| I. | 44·48 | 36·24 | 2·18 | 0·44 | 0·19 | 2·03 | 14·12 | 99·68 |
| II. | 78·29 | 15·00 | 4·85 | 1·77 | 0·47 | — | — | 100·38 |
| III. | 69·27 | 19·42 | 0·84 | 1·30 | 10·01 | — | — | 100·84 |

L. J. S.

A Sodiferous Pyroxene from the Neighbourhood of Oropa in the Biellesi. By FERRUCCIO ZAMBONINI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 240—244).—The author describes a pale greenish pyroxene found in masses 7 or 8 centimetres long and 1 cm. wide, which together with granite, amphibole and broad plates of white mica, forms numerous nodules and lenticular masses distributed in the micaceous schist on the southern slope of the Cima Cucco to the east of Oropa. The crystalline system is shown to be monoclinic, not triclinic as Arzruni suggested on optical evidence. The chemical composition of the mineral is as follows :

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | MgO. | Na ₂ O. | K ₂ O. | Loss on ignition. | Total. |
|--------------------|----------------------------------|----------------------------------|-------|------|--------------------|-------------------|----------------------|--------|
| 53.54 | 14.79 | 5.14 | 14.83 | 3.59 | 7.73 | 0.27 | 0.28 | 100.17 |

These numbers agree well with the formula :



The specimen hence belongs to that group of pyroxenes which, owing to the large proportion of sexavalent elements and of sodium, may be termed jadeitoid pyroxenes.

T. H. P.

Some Iowa Dolomites. By NICHOLAS KNIGHT (*Amer. J. Sci.*, 1901, [iv], 11, 244—246).—Analyses are given of seven dolomitic limestones from Iowa. Five of them closely approach typical dolomite ($\text{CaCO}_3, \text{MgCO}_3$) in composition, and the only impurities present are small amounts of ferric oxide, alumina, and silica.

L. J. S.

Koswite, a new pyroxenite from the Urals. By LOUIS DUPARC and FRANCIS PEARCE (*Compt. rend.*, 1901, 132, 892—894).—Associated with olivine-gabbros in the Solikamsk district, near the source of the Kosswa river, is a new type of basic eruptive rock to which the name koswite is given. It consists of diallage, olivine, hornblende, magnetite and picotite. The magnetite is present in large amount between the other constituents, and corresponds with the quartz in granite. As the magnetite decreases in amount and becomes idiomorphic, there is a passage from koswite to ordinary pyroxenite. Chemical analyses of the rock are given.

L. J. S.

Perovskite from Emarese in Val d'Aosta. By FEDERICO MILLOSEVICH (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 209—211).—The author describes crystals of perovskite found in the asbestos caves of Emarese, which are at a height of about 1200 metres. The crystals are cubic in habit having in some cases a side 3 mm. long, and are accompanied by chlorite and magnetite. They resemble closely the crystals found in the Urals, and have a composition agreeing almost exactly with the formula CaTiO_3 , traces of MgO being also present.

T. H. P.

Presence of Nitrides, Argonides, Arsenides, and Iodides in the Crystalline Rocks. By ARMAND GAUTIER (*Compt. rend.*, 1901, 132, 932—938. Compare this vol., ii, 14).—Specimens of mica-

schist, basalt, granulite, and several varieties of granite when finely powdered and heated to redness, or boiled with acids, yield nitrogen accompanied by traces of argon, but no helium. These gases are derived from the nitrides and argonides present in the plutonic rocks; the former compounds give up only a portion of their nitrogen in the free state, the remainder being eliminated in the form of ammonia, which remains in the acid. In order to estimate the quantity of ammonia evolved from a rock specimen, the finely powdered substance is digested for some time at 100° with syrupy phosphoric acid diluted with 2 to 3 vols. of water. About 1 to 2 per cent. of the total nitrogen of these rocks exists in the form of iron nitrides; these substances are extracted from the crushed mineral by the aid of a magnet.

Iodine is also present in small quantities in the granite; it is eliminated by distilling the mineral with pure concentrated sulphuric acid, and estimated by the author's method (*Compt. rend.*, 1899, 128, 644). This element is very generally accompanied by arsenic; all the samples of granite examined contain the latter substance. The ophitic rock of Villefranche, however, does not contain either of these elements. The gases evolved from the earth's crust, whether dissolved in the natural mineral waters or issuing into the atmosphere, are probably formed by the action of water at high temperatures on the silicates, nitrides, carbides, sulphides, arsenides, and other accessory constituents of the igneous rocks. (Compare this vol., ii, 171, 322).

G. T. M.

Mineral Constituents of Dust and Soot from Various Sources. By W. NOEL HARTLEY and HUGH RAMAGE (*Proc. Roy. Soc.*, 1901, 68, 97—109).—Soot is found to contain nickel, so that the presence of this metal does not prove that the dust from the clouds comes from other than a terrestrial source. Examination of a dust which fell during a calm night in November 1897, showed that its composition was quite unlike that of volcanic dust, or of dust from various chemical and metallurgical works; it is magnetic, very regular in composition, and probably of cosmic origin. The authors draw attention to the wide distribution of gallium in small traces; it occurs in all aluminous minerals, in flue dust from various sources, in soot and atmospheric dust, as well as in many iron ores.

J. C. P.

Meteoric Iron from Kokstad, Bethanien, and Muchachos. By EMIL W. COHEN (*Chem. Centr.*, 1901, i, 851; from *Mitt. nat. Ver. Neuvorpommern u. Rügen*, 1900, 1—43).—The specimens of meteoric iron from Kokstad, Bethanien, and Muchachos in the Vienna Natural History Museum have been again examined. The nickel-iron does not form a homogeneous mass but is traversed by extremely narrow, lustrous, zig-zag seams and the specimens contain olivine and plagioclase. The Carleton meteoric iron contains 94·07 per cent. of nickel-iron, 1·04 of schreibersite, 0·07 of lawrencite, and 4·82 of olivine; its bulk analysis is given under I, and that of the olivine isolated from it by means of copper-ammonium chloride under II. It thus appears to be a forsterite mixed with a small quantity of monticellite silicate. The mass of the olivine is found to be practically free from iron when the

opaque portions contained in it are taken into account. The Muchachos iron belongs to a special group of the ataxites.

| | Fe. | Ni. | Co. | Cu. | Cr. | C. | S. |
|-----|-------|------|------|------|------|------|--------|
| I. | 84.56 | 8.89 | 1.36 | 0.03 | 0.02 | 0.04 | trace. |
| II. | — | — | — | — | — | — | — |

| | Cl. | P. | SiO ₂ . | FeO. | MgO. | CaO. | Olivine and residue. |
|-----|------|------|--------------------|------|-------|-------|----------------------|
| I. | 0.04 | 0.16 | 1.72 | — | 0.59 | trace | 3.68 |
| II. | — | — | 43.29 | 0.52 | 54.92 | 1.13 | — |

E. W. W.

Meteorite Stones which fell at Zomba, British Central Africa. By LAZARUS FLETCHER (*Min. Mag.*, 1901, 13, 1—37).—On January 25th, 1899, a single loud detonation was accompanied by the fall of several meteoric stones over an area of about 9 by 3 miles near Zomba, in British Central Africa. The largest of the ten stones collected weighs 5 lbs. 12½ ozs. Sp. gr. 3.545. As seen under the microscope, the structure is crystalline, and there are few chondrules. From detailed analyses of the portion attracted by a magnet and of the unattracted portion, decomposed and undecomposed by hydrochloric acid, the percentage mineralogical composition of the stone is deduced as follows:

| Nickel-iron. | Olivine. | Enstatite. | Oligoclase. | Troilite. | Chromite. |
|--------------|----------|------------|-------------|-----------|-----------|
| 8.61 | 42.44 | 34.80 | 8.77 | 4.85 | 0.53 |

The calculated percentage compositions of the enstatite, of the oligoclase, and of the olivine are given under I, II, and III respectively.

| | SiO ₂ . | Al ₂ O ₃ . | FeO. | MnO. | CaO. | MgO. | Na ₂ O. | K ₂ O. | Sp. gr. |
|------|--------------------|----------------------------------|-------|------|------|-------|--------------------|-------------------|---------|
| I. | 55.64 | — | 12.76 | 0.49 | 3.80 | 27.31 | — | — | 3.314 |
| II. | 61.55 | 24.04 | — | — | 5.61 | — | 7.90 | 0.90 | — |
| III. | 38.25 | — | 23.23 | 0.45 | 1.18 | 36.89 | — | — | — |

Full details are given of the methods of analysis and of the calculation of the results. In chemical composition and structure, the Zomba meteorite is very similar to that from Linn County, Iowa.

L. J. S.

Physiological Chemistry.

Action of Isotonic Solutions of Chlorides and Sugar on Frogs' Eggs. By MADAME RONDEAU-LUZEAU (*Compt. rend.*, 1901, 132, 997—999).—The eggs of *Rana fusca* were exposed for varying periods to the action of solutions of sugar and salt of varying strengths. On unfertilised eggs, the results are practically negative; after fertilisation, the eggs appear to be more sensitive to the physical action of the solutions; the effects described are very irregular.

W. D. H.

Comparative Value of Saline and Saccharine Solutions in experimental Teratogenesis. By E. BATAILLON (*Compt. rend.*, 1901, 132, 852—854).—Solutions of salt, sugar, and other substances, if employed in isotonic quantities, determine the same changes in the development of frog embryos, and the abnormalities observed depend on the plasmolysis which such solutions engender. W. D. H.

A New Histon from Fish-sperm. By ROBERT EHRSTRÖM (*Zeit. physiol. Chem.*, 1901, 32, 350—354).—The testicles of the fish *Lota vulgaris* (a member of the cod family) contain histon instead of protamine. Histon has been previously described in the sperm of other fishes, and it is considered probable that in process of ripening it forms the source of the protamine. The following table compares the percentage amounts of certain products obtained from three varieties of histon :

| | Lota-histon. | Cod-histon. | Thymus-histon. |
|------------------|--------------|-------------|----------------|
| Ammonia | 0.66 | 0.74 | 1.66 |
| Histidine | 2.85 | 2.34 | 1.21 |
| Lysine | 3.17 | 8.30 | 7.70 |
| Arginine | 12.00 | 15.22 | 14.36 |

W. D. H.

Nature of Pepsin. By MARCELLUS NENCKI and NATALIE SIEBER (*Zeit. physiol. Chem.*, 1901, 32, 291—319).—Gastric juice was obtained by the Pawloff-Schoumoff-Simanowski method, and from it pepsin was precipitated by cooling to 0°. The product appears to be identical with that obtained by Pekelharing's method (*Abstr.*, 1897, ii, 60), or by precipitation with ammonium sulphate. The molecules of pepsin are described as "labile" and "giant," consisting of nucleo-proteid, united to iron, phosphoric acid, pentose, lecithin, and chlorine. The various actions of gastric juice, namely, its peptonising action, milk-curdling action, and the formation of an insoluble material, plastein, from proteoses, are all attributed to this material. W. D. H.

Mett's Method of estimating Peptic Activity. By ALEXANDR A. SAMOJLOFF (*Pflüger's Archiv*, 1901, 85, 86—89).—Mett's method consists in measuring the decrease in length of cylinders of egg white coagulated in capillary tubes, which occurs under the influence of artificial digestive juices. The method is recommended as an accurate one. The law that peptic activity is proportional to the square root of the amount of pepsin present is shown to be true, except when the amount of pepsin is very great; with high concentrations, the figures found are less than those calculated.

Similar work by A. Walter (*Inaug. Diss. Petersburg*, 1897) has shown that the same law holds for trypsin. W. D. H.

Alcohol as a Stimulant of Gastric Secretion. By C. RADZIKOWSKI (*Pflüger's Archiv*, 1901, 84, 513—526). **Two Pure Peptogens.** By FR. R. MARK-SCHNORF (*ibid.*, 85, 143—148).—Substances which stimulate gastric secretion may be divided into those which increase the flow of the juice (peptagogues), and those which increase the secretion of pepsin (peptogens) (compare Herzen, this vol., ii, 323). Alcohol has simply the former effect; it acts best if given by

the mouth, but also to a less degree by the rectum. Its occurrence in the blood in small quantities does not hinder the change of propepsin into pepsin under the influence of Schiff's peptogens.

Inulin and glycogen are exclusively peptogenic in their action, without a trace of peptagogue activity; pure dextrin is neither.

W. D. H.

Action of Alcohol on the Gastric Secretion. By ALBERT FROUIN and M. MOLINIER (*Compt. rend.*, 1901, 132, 1001—1003).—Experiments made on dogs show that alcohol promotes the secretion of gastric juice. This phenomenon is due to the specific action of the substance on the nervous system, not merely to local action or to the irritation of the nerve endings of the alimentary track, similar results being obtained whether the alcohol is introduced through the mouth or directly injected into the intestine.

G. T. M.

Variation of the Quantity of Thiocyanate contained in Human Saliva and its Causes in Health and Disease. By JUL. A. GROBER (*Chem. Centr.*, 1901, i, 839—840; from *Deut. Arch. klin. Med.*, 69, 243—257).—Potassium thiocyanate is found in the human body only in the saliva. It is not formed by the decomposition of the saliva, but is actually secreted, and the quantity diminishes with the duration of the secretion. The quantity present in the saliva is not affected by change of diet in the case of healthy persons or by the use of tobacco by non-smokers, but it appears to increase after administering extremely small doses of hydrocyanic acid. The secretion of the thiocyanate is probably dependent on the condition of the organism in respect to the albumin decomposed and utilised, and where this is small in amount, as in severe cachectic cases, little or no thiocyanate is secreted.

E. W. W.

The Functions of Bile as a Solvent. By BENJAMIN MOORE and WILLIAM H. PARKER (*Proc. Roy. Soc.*, 1901, 68, 64—76).—Bile acts as a solvent in two ways: (1) it dissolves lecithin, and, to a less extent, cholesterol; it thus aids the excretion of these otherwise insoluble substances by the liver cells, and their carriage to the intestine; (2) it dissolves both free fatty acids and soaps, and thus renders the absorption of these substances easier. The solvent properties are chiefly due to the bile salts, but in the case of the fatty acids and soaps the amount dissolved is greatly increased by the simultaneous presence of lecithin.

W. D. H.

A Proteolytic Enzyme in the Spleen. By SVEN G. HEDIN and S. ROWLAND (*Zeit. physiol. Chem.*, 1901, 32, 341—349).—The juice expressed from the spleen of the ox, sheep, and pig contains a proteolytic enzyme, which works best in an acid medium. Whether the enzyme is present as such, or as a zymogen, was not determined; the enzyme itself is not trypsin.

W. D. H.

A Type of Reaction by which Sodium Carbonate and Hydrochloric Acid may be formed in the Animal Organism. By THOMAS B. OSBORNE (*Amer. J. Physiol.*, 1901, 5, 180—181).—Crystalline globulin (edestin) is a mixture of salts of proteid, chiefly hydrochlorides and sulphates. Edestin was suspended in water, and neutralised by

potassium hydroxide. It was then washed with water and dissolved in sodium chloride solution, carbon dioxide was then passed through the diluted solution, and the precipitated edestin was washed, dehydrated, and dried. Solutions of this in water or strong sodium chloride solution are acid. Fifteen grams of this were dissolved and treated with 28.5 c.c. of decinormal potassium hydroxide; the edestin so precipitated was washed with water, the filtrate and washings contained 0.23 gram of solid residue, of which 0.022 was organic, and 0.212 inorganic (KCl , 0.199; K_2SO_4 , 0.015). Thus, more than 93 per cent. of the potassium added was recovered as chloride, and from the edestin there had precipitated 0.097 gram of hydrochloric acid, or 0.072 per cent. of the protein. Corresponding with this quantity of hydrochloric acid, 0.1417 gram of sodium carbonate must have been produced in the salt solution by the carbon dioxide. It is considered probable that by a similar reaction, both sodium carbonate and hydrochloric acid may be formed from sodium chloride in the organism, since there is always sodium chloride and proteid matter present when carbon dioxide is produced in the tissues.

W. D. H.

Theory of Proteid Digestion. By W. W. SAWJALOFF (*Pflüger's Archiv*, 1901, 85, 171—225).—The theory advanced is that the object of peptonisation is not to render proteid matter easier of absorption, for side by side with this process there is another which begins while the proteid is still within the alimentary canal, and which is a change in the reverse direction, building up proteids of large molecular weight from the products of peptonisation. This action is attributed to the rennet ferment. It is pointed out that rennet is not confined to the gastric juice of animals which take milk; it is, for instance, found in fishes. Gastric juice in virtue of this ferment is able to cause the formation of a precipitate or clot in solutions of proteoses and peptone. The name *plastein* has recently been given to this insoluble substance. Much of the present paper is taken up with a description of the properties of plastein and the conditions of its formation in acid and alkaline media; its percentage composition appears to be about the same whatever proteid is subjected originally to digestion; its properties are much the same as those of Kühne's anti-albumid. A number of different proteids are digested, but the varieties of proteid found in the blood are constant. Pepsin-hydrochloric acid breaks down proteid of all kinds into simpler substances, and from these a plastein of constant composition is resynthesised.

W. D. H.

The Absorption of Artificially Coloured Fats. By LUDWIG HOFBAUER (*Pflüger's Archiv*, 1901, 84, 619—627); by SIGM. EXNER (*ibid.*, 628—635); by EDUARD PFLÜGER (*ibid.*, 85, 1—58).—Polemical. The two first named authors maintain that the phenomena of absorption of coloured fats support the emulsion theory. In the third paper of the series, the author maintains that the methods of experiment are faulty, and that the opposite theory is correct.

W. D. H.

Fat Digestion. By SIEGFRIED ROSENBERG (*Pflüger's Archiv*, 1901, 85, 152—170).—In order to discover whether soaps are completely absorbed, they were introduced directly by a fistulous opening into

the bowel in dogs, and the fæces examined. The results obtained do not support the Cohnstein-Pflüger theory that all fat is absorbed in the form of soap, and that saponified fat requires bile for its absorption, as much as neutral fat and fatty acid do. W. D. H.

Action of Carbon Dioxide on Blood Vessels. By WILLIAM M. BAYLISS (*Proc. physiol. Soc.*, 1901, xxxii—xxxiii).—Observations were made in the blood vessels of the frogs which were perfused with Ringer's solution, in some experiments saturated with air, in others with carbon dioxide. Dilatation about equal to that produced by lactic acid (1 in 10,000) was observed. In mammals, no local action could be detected. W. D. H.

Sugar in Normal Hen's Blood. By S. SAITO and K. KATSUYAMA (*Zeit. physiol. Chem.*, 1901, 32, 231—234).—The amount of sugar in normal hen's blood is about 0.2 per cent. This is more than in dogs and rabbits. The sugar was identified as dextrose. W. D. H.

Febrile Changes in the Chemical Composition of Blood. By KARL RITTER VON STEJSKAL (*Chem. Centr.*, 1901, i, 845; from *Zeit. klin. Med.*, 42, 309—323).—The blood of fever patients has been found to contain less albumin, fat, cholesterol, iron, and chlorine, and to yield a smaller quantity of dry substances than normal blood. On the other hand, the quantities of water, calcium, potassium, and ash were in excess of the usual amount, whilst the amounts of lecithin and sodium were normal. The blood serum showed a decrease of albumin, substances soluble in ether, chlorides, and dry substances, but contained a greater quantity of potassium, and yielded a larger ash. The fact that in the febrile state the red corpuscles contain less albumin, lecithin, and cholesterol, but are richer in water and salts, can only be due to imbibition of solutions containing salts (plasma) and especially chlorides. The red corpuscles had increased in weight, whilst the plasma had correspondingly decreased. E. W. W.

The Ammonium Sulphate Method of separating the Proteids of Horse-serum. By W. POPPLEWELL BLOXAM (*Proc. physiol. Soc.*, 1901, xxxiii—xxxv).—Quantitative estimations show that the globulin of horse-serum loses weight on re-solution and reprecipitation by half-saturation with ammonium sulphate. This tends to show that either the method is faulty, or that globulin is changed into albumin by treatment with the salt. W. D. H.

Coagulating Properties of Mucin. By ALBERT CHARRIN and MOUSSU (*Compt. rend.*, 1901, 132, 578—580).—Experiments are given which show that solutions of 'mucus' collected mostly from the respiratory tract, when injected into animals produce intravascular clotting of the blood. W. D. H.

Formation of Oxalic Acid in the Human Body. By N. STRADOMSKY (*Virchow's Archiv*, 1901, 163, 404—440).—The oxalic acid of the urine has a double origin: (1) from the food; (2) as a result of normal metabolism. On a mixed diet containing practically no oxalic acid, the 24 hours' urine contains 0.015 gram. Increase of pro-

teid food increases the amount; creatine is possibly an intermediate substance; gelatin increases the amount. If oxalic acid is given by the mouth, 35.3 per cent. reappears in urine and faeces. Of the remainder, some, doubtless, is broken up by bacteria in the intestine, and some is oxidised and leaves the body in other ways. W. D. H.

Formation of Lactic Acid in the Organism. By S. SAITO and K. KATSUYAMA (*Zeit. physiol. Chem.*, 1901, 32, 214—230).—The experiments were made on hens; the normal blood of these animals contains 0.02 per cent. of *d*-lactic acid. After extirpation of the liver, the amount rises considerably, and passes into the urine. The same is true when oxidation is diminished, as in poisoning by carbon monoxide. W. D. H.

Mineral Composition of the Human Foetus and New-born Child. By LOUIS HUGOUNENQ (*Ann. Chim. Phys.*, 1901, 22, [vii], 370—393. Compare Abstr., 1899, ii, 503, 682; 1900, ii, 418, 490).—The generalisations deduced from the analyses tabulated in this paper have already been published. G. T. M.

Composition of Fatty Substances in the Animal Organism. By VALDEMAR HENRIQUES and C. HANSEN (*Bied. Centr.*, 1901, 30, 182—186; from *Overs. K. dansk. Videnskab. Selskabs Forhandl.*, 1900, No. 3, 225—241. Compare Abstr., 1900, ii, 668).—The iodine numbers and solidifying points were determined in fat from different parts of the bodies of different animals. In the case of dogs, horses, bullocks, pigs, camels, and geese, it was found that the amount of liquid (unsaturated) fatty acids decreases as the position of the fat approaches the warmest parts of the body.

The fat in the back of a well-fed pig can be readily separated into two layers; in every case, the outer layer showed a higher iodine number, and a lower solidifying point, than the inner layer. Similar results were obtained when the two layers were each subdivided. The fat of pigs fed with maize showed higher iodine numbers than when they were fed with barley, but the difference in feeding did not affect the relation between the inner and outer fat. The iodine numbers of the kidney fat were still lower than those of the deeper portions of the fat on the back. Fat from the hump of a camel gave similar results.

The fat from all parts of seals has a very high iodine number (150—160), due to fatty acids with very little hydrogen. By cooling the very fluid fats at 3° for some days, separations of crystals were obtained, the greatest amounts being in the fats from the lowest layers.

In the case of dolphin fat, the iodine numbers increase with the depth of the fat. The melting point also increases, but in this case the lower melting point of the surface fat is not due to olein, but to valerin.

Experiments were made with pigs under different conditions of temperature; the one was kept in a room at 30—35°, the second was kept at 0°, but with a sheep-skin (with the wool) sewn round it, and the third was kept at 0° in its natural condition. The surface fat of the pig kept at the lowest temperature was found to contain the most

olein, whilst that of the pig with the woolly cover showed the lowest iodine number and the highest solidifying point.

Determinations of the temperature of the different layers of fat showed considerable differences. The following results were obtained: At 1 cm. under the skin, 33.7° ; at 2, 3, and 4 cm., 34.8° , 37.0° , and 39.0° respectively.

N. H. J. M.

Complete Removal of the Suprarenal Glands. By BEN JAMIN MOORE and C. O. PURINTON (*Amer. J. Physiol.*, 1901, 5, 182—190).—In the cat, complete removal of the suprarenal glands is always, in goats generally, fatal. The chief symptoms are extreme muscular weakness and rapid, shallow breathing. In cats, rapid clonic convulsions were observed. Death is due to respiratory failure, and in three out of seven cases ante-mortem clotting in the right heart, and the vessels connected with it, was observed.

W. D. H.

Methods for determining the Limits of Olfactory Sensibility. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1901, 22, [vii], 460—464).—This note contains a description of an apparatus consisting of a series of large flasks in which air containing a definite quantity of some odoriferous substance may be quantitatively diluted until the odour ceases to be perceptible. The atmosphere of the first flask of the series was saturated with iodoform vapour and then contained 1.1 mg. of this substance in 4 litres of air; 40 c.c. of this atmosphere were then introduced into the second flask, which was then found to have a distinct odour of the compound. After two repetitions of the process of dilution, the odour could not be distinguished in 1 c.c. of the air of the fourth flask. The odour of musk, however, persists even when the dilution is one thousand times greater than that of the preceding experiment.

G. T. M.

Distribution of Galactase in different Species of Mammalia. By S. MOULTON BABCOCK, H. L. RUSSELL, and ALFRED VIVIAN (15th *Ann. Rep. Agric. Expt. Stat. Univ. Wisconsin*, for 1897—1898, 93—97).—Galactase was found to be present, not only in cow's milk but in human milk and the milk of sheep, goats, pigs, mares, and a half-bred buffalo. Owing to the varying chemical composition of the different milks, the amount of galactase could not be determined.

N. H. J. M.

Distribution of Galactase in Cow's Milk. By S. MOULTON BABCOCK, H. L. RUSSELL, and ALFRED VIVIAN (15th *Ann. Rep. Agric. Expt. Stat. Univ. Wisconsin*, for 1897—1898, 87—92).—The estimation of the amount of galactase, measured by the amount of soluble proteids formed, showed but little difference at various stages in the period of lactation. During the colostrum period, the amount of soluble proteids seemed to be slightly increased at the beginning, as compared with normal milk, five days after calving, but the reason for this difference is uncertain.

The milk taken from different cows at the same period of lactation was found not to vary to any extent as regards the amount of galactase.

N. H. J. M.

Influence of the Amount of Water consumed on the Secretion of Milk. By B. KOCH (*J. Landw.*, 1901, 49, 61—88).—Increased consumption of water, induced by adding salt to the food of cows, does not increase the yield of milk or cause any considerable diminution in the amount of dry matter in the milk. In some cases, when the amount of salt is not excessive, individual cows may yield rather more milk than without salt; the effect on other cows, may, however, be just the opposite. N. H. J. M.

Excretion of Phosphorus during Inanition. By FRIEDRICH N. SCHULZ and J. MAINZER (*Zeit. physiol. Chem.*, 1901, 32, 268—277).—The principal proteid constituent of protoplasm contains phosphorus, and this element is most abundant in the nucleus, which is the most important part of a cell. Experiment appears to show that in hunger the phosphorised constituents of the cell are the most protected. The ante-mortem rise of nitrogenous excretion may be regarded as a sparing action of this kind, but in the few experiments recorded, the proportion of nitrogen to phosphorus was very variable, and did not bear out the view. W. D. H.

Excretion of Nitrogen after Extirpation of the Liver. By S. LANG (*Zeit. physiol. Chem.*, 1901, 32, 320—340).—The urine was examined which was passed in birds during the few hours that intervened between removal of the liver and death. The nitrogen was estimated in three fractions: (1) That which can be driven off by magnesia; this is mainly derived from the ammonia, but also includes a small amount from urea. This amount was much increased. (2) That present after the removal of the first fraction, which is precipitated by phosphotungstic acid. This corresponds to the uric acid and purine bases. Administration of alkali does not, under the conditions of these experiments, raise the amount of uric acid. (3) The nitrogen left after the separation of fraction 2 is derived from amino-acids, urea, and creatine. Full details of numerous experiments are given. W. D. H.

Influence of certain Diuretics on the Excretion of Alkalis. By K. KATSUYAMA (*Zeit. physiol. Chem.*, 1901, 32, 235—240).—Urea and diuretin both cause an increase in the amount of chlorides and alkalis (especially sodium salts) in the urine. In this they resemble theine. The experiments were made on rabbits in a state of hunger. W. D. H.

Excretion of Kynurenic Acid. By WILLIAM J. GIES (*Amer. J. Physiol.*, 1901, 5, 191—195).—In a dog no kynurenic acid was found when the animal was in normal equilibrium. If the equilibrium was upset and proteid katabolism increased by dosage with tellurium, the acid appeared. The uric acid was constant throughout, and kynurenic acid is not associated with intestinal putrefaction. W. D. H.

Indoxylic Origin of certain Red Colouring Matters of Urine (Indirubin). By LOUIS MAILLARD (*Compt. rend.*, 1901, 132, 990—992).—A normal urine, containing notable quantities of indigo-yielding

substances when boiled to destroy enzymes, and treated with hydrochloric acid and ferric chloride, gives a blue colouring matter (indigo). When the boiled urine is first digested with the acid, and only subsequently treated with the oxidising agent, it yields a red colouring matter. This product, which, unlike the red pigment, urochrome, is soluble in chloroform, seems identical in its properties with the indirubin derived from the *Indigofera*.
G. T. M.

Analysis of Liquid obtained from a Hydatid Cyst of the Liver. By F. MALMÉJAC (*J. Pharm.*, 1901, [vi], 13, 406—407).—The liquid (1012 c.c.) was perfectly colourless, limpid, and of acid reaction, and contained 13 grams of solid matter per litre, of which sodium chloride forms 5.8 grams, urea 2 grams, and calcium oxide 1 gram. In addition, small quantities of serum-albumin, sulphates, phosphates, and acetone are present.
K. J. P. O.

Action of Chloroform and Ether on the Nerve-cells of Dogs. By HAMILTON WRIGHT (*J. Physiol.*, 1901, 26, 362—365. Compare this vol., ii, 180).—The experiments support those previously recorded, and show that if anaesthesia is prolonged to nine hours in dogs, even the nucleus loses much of its affinity for basic aniline stains. After the anaesthesia passes off, recovery is absolute.
W. D. H.

Action of Nicotine on Nerve-cells. By J. HERBERT PARSONS (*Proc. Physiol. Soc.*, 1901, xxxviii—xxxix).—After nerve-cells have been placed in 1 per cent. aqueous solutions of nicotine for an hour, they undergo no histological change. This supports the view that the alkaloid acts on the synapse that surrounds the cell. A longer immersion in the solution, or the use of stronger solutions for shorter periods, produces chromatolysis.
W. D. H.

Physiological Action of Aspirin. By H. SINGER (*Pflüger's Archiv*, 1901, 84, 527—546).—Aspirin (o-acetoxybenzoic acid) does not increase the flow of urine, but somewhat raises the total output of solids. The total nitrogen is not affected. In rabbits (2 experiments) the consumption of oxygen is lessened from 14 to 17 per cent.; in one experiment, it was increased by 9 per cent. It causes in these animals leucocytosis, and an increased output of uric acid and purine bases. The amount of urobilin in the urine is somewhat diminished. The increase of total solids in the urine is principally due to a rise of phosphates and sulphates. The ethereal hydrogen sulphates are not affected.
W. D. H.

Physiological Action of Guanylic Acid. By IVAR BANG (*Zeit. physiol. Chem.*, 1901, 32, 201—213).—Guanylic acid intravenously injected in dogs produces great delay in blood-clotting, irregularity and disturbance of respiration, a fall of arterial blood pressure, chiefly due to dilatation of peripheral vessels, and an alkaline reaction of the urine. Albuminuria is generally present, but sugar in the urine was only found in one experiment. Injection of nucleo-proteid produces very similar effects, except that the urine is not rendered alkaline, and albuminuria is not a marked effect. The urine always contains dextrose, but no β -hydroxybutyric acid or acetone.
W. D. H.

Physiological Action of three Poisonous Toadstools. By WILLIAM S. CARTER (*Amer. J. Physiol.*, 1901, 5, 158—174).—The experiments were made with fungi dried at 40°, or with glycerol or alcoholic extracts of the fresh growth. *Amanita muscaria* produces cardiac inhibition in frogs and mammals by acting on the inhibitory mechanism of the heart itself, vaso-dilatation, arrest of respiration, salivation, contracted pupils, occasionally vomiting and purging, but never convulsions. Atropine is of antidotal value, but the fungus appears to contain, besides muscarine, some poison or poisons which are not antagonised by atropine. *A. verna* or *bulbosa* causes less effect on the heart; its chief action is to dilate blood vessels; vomiting and purging are more frequent than with *A. muscaria*, and convulsions were frequently observed due to action on the spinal cord. *A. phalloides* has a very similar action on the circulation; when cardiac inhibition occurs it is due to an effect on the cardio-inhibitory centre. There is but little action on the spinal cord. Histological examination of the nerve-cells in all three cases showed no change in them.

W. D. H.

Behaviour of Pyrimidine Compounds in the Animal Organism. By H. STEUDEL (*Zeit. physiol. Chem.*, 1901, 32, 285—290).—The different intermediate products which Behrend and Roosen employed in the synthesis of uric acid (*Abstr.*, 1888, 581) have been separately given to a fox terrier bitch in its food, in order to determine what alterations these undergo in the animal organism, and whether any of them can give rise to a purine derivative. Methyluracil is mostly obtained in the urine in an unaltered condition. Nitrouracil-carboxylic, isobarbituric, and isodialuric acids are completely destroyed, whereas nitrouracil passes through unaltered. Traube's 2:4-diamino- and 2:4:5-triamino-6-oxypyrimidine have a toxic action, and both are fatal in doses of 0.2 and 0.1 gram respectively.

J. J. S.

Maltosuria in a Diabetic Patient. By RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1901, 132, 610—613).—Analyses of a specimen of diabetic urine are given which support the view that in this case, as in some others which have been met with, the sugar was a mixture of dextrose and maltose.

W. D. H.

Treatment of Carbon Monoxide Poisoning by Oxygen at Atmospheric Pressure. By NESTOR GRÉHANT (*Compt. rend.*, 1901, 132, 574—576).—In dogs, it was found that with an animal on the point of death from carbon monoxide poisoning, and then made to breathe air containing 90 per cent. of oxygen, the blood at the end of an hour contains 18.8 of oxygen and 1.1 of carbon monoxide per cent. by volume. If ordinary air is used, the numbers are respectively 16.6 and 4.5.

W. D. H.

Chemical and Microbiological Investigations on the Salting of Herrings. By SIGVAL SCHMIDT (*Bied. Centr.*, 1901, 30, 195—198; from *Rep. on Norwegian Fishery and Marine Investigations*, 1, No. 8, 1—27, Christiania, 1900).—In addition to sodium chloride, the liquid in which herrings have been salted contains potassium, calcium, magnesium, sulphuric acid, and a considerable amount of

phosphoric acid derived from the fish; solutions 2—4 weeks and $2\frac{1}{2}$ —5 years old contained 1.6 and 1.9—2.1 per thousand of P_2O_5 . No nitric or nitrous acid could be detected. The amount of nitrogen found after a few days' salting was about 0.1 per cent.; in old solutions ($2\frac{1}{2}$ and 5 years), the amounts of nitrogen were 0.9 and 1.2 per cent. In fresh solutions, most of the nitrogen is in the form of amides, but after a year albumose, peptone, and (in increasing amount) tryptophan are found. The genuine albumin of the liquor consists to only a slight extent of globulin, and contains neither nuclealbumin nor histon; it consists of at least two substances. The greater part is precipitated by 0.2 per cent. acetic acid in absence of sodium chloride, whilst in saturated salt solutions the precipitation is complete.

The amide nitrogen in the solutions represents more than 75 per cent. of the total nitrogen; only a small portion is present as xanthine and purine bases.

The white sediment deposited during salting consists partly of optically inactive, very lustrous needles, readily soluble in ether.

Most of the microbes present in the salt solutions are bacteria; even old solutions (5 years) contain some hundreds per c.c. The solutions become sterile if the fish is removed.

Analyses of herrings salted for various periods are given.

N. H. J. M.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation of Sugars by *Bacillus Coli Communis* and Allied Organisms. I. By ARTHUR HARDEN (*Trans. Jenner Inst. of Preventive Medicine*, 1899, 2, 126).—The gas produced from dextrose by *Bacillus coli communis* under anaerobic conditions consists of carbon dioxide and hydrogen, the ratio in which these gases are present varying from 1:1 to 1:1.3. This gas, and that evolved from nutrient gelatin under similar conditions, contain no methane. The lactic acid produced from dextrose by the organism employed in presence of peptone water was a mixture of *l*-lactic acid with a considerable proportion of the inactive form, whereas in presence of beef-broth it consisted almost entirely of the inactive form. A. H.

Bacteria which destroy Nitrates and their Action in the Soil. By KRENZ and MAX GERLACH (*Bied. Centr.*, 1901, 30, 228—232; from *Jahresber. Landw. Versuchs-Stat. Jersitz-Posen*, 1898—1899, p. 3).—The results of pot experiments with oats showed that addition of carbonaceous food (a mixture of xylan, glycerol, and sodium lactate) greatly increased denitrification; fresh cow dung had practically no effect in presence of nitrate. Peat does not promote denitrification.

Cow urine greatly increased the yield of buckwheat; addition of carbonaceous matters diminished the yield; but the loss of nitrogen was much less than that which takes place when nitrate and carbonaceous matter are applied together.

Farmyard manure (fresh and old) increased the yield of barley, but less than nitrate. The yield obtained with farmyard manure and nitrate was greater than with nitrate alone.

The conclusion is drawn that whilst fresh cow dung is without effect on denitrification, farmyard manure which contains more or less carbonaceous food, suitable for denitrifying microbes, may act both favourably and unfavourably at the same time. N. H. J. M.

Chlorophyllous Assimilation without Living Organisms. By JEAN FRIEDEL (*Compt. rend.*, 1901, 132, 1138—1140).—By pressing leaves of spinach with glycerol, and filtering, a very clear, yellowish liquid was obtained which contained the soluble matter of the leaves. The liquid is not capable of assimilating carbon dioxide either with or without light. The green powder obtained by drying similar leaves at 100° was also found to be incapable of assimilation. When, however, the green powder is added to the solution and exposed to light, assimilation takes place. Similar results were obtained when the glycerol extract was precipitated with alcohol; on adding water and chlorophyll to the precipitate the mixture was found to have the power of absorbing carbon dioxide and liberating oxygen. The liquid is rendered inert by boiling. N. H. J. M.

Are Lower Chlorophyllous Algæ able to assimilate Free Nitrogen and to increase the amount of Nitrogen in the Soil? By W. KRÜGER and W. SCHNEIDEWIND (*Bied. Centr.*, 1901, 30, 217—218; from *Landw. Jahrb.*, 1900, 29, 771).—The results of experiments with *Stichococcus* (8), *Chlorella vulgaris* (5), *C. protothecoides* (4), and *Chlorothecium* (6 varieties), which extended over 328 to 440 days, showed that no assimilation of free nitrogen took place. It is probable that none of the lower algæ can fix nitrogen.

Some groups of algæ grew most luxuriantly when supplied with organic nitrogen; others thrive equally well in presence of inorganic nitrogen compounds.

Algæ under natural conditions are probably favourable to the growth of bacteria which fix free nitrogen. N. H. J. M.

Influence of Nutrition on the Secretion of Enzymes by *Monilia Sitophila*. By F. A. F. C. WENT (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 489—502).—The mould *Monilia sitophila* is employed in West Java for decomposing arachis-seed cake; it also occurs on putrefying bread and wheat flour and on dead leaf-sheaths of the sugar cane. The mould has a bright orange-red colour. The pigment dissolves in alcohol, ether, benzene, chloroform, &c., yielding golden-yellow to brownish-red solutions with a faintly green fluorescence, the absorption spectrum of which shows a dark zone, embracing the whole of the blue and violet portions from about F. The pigment is only produced in presence of light (the blue and violet rays); in light

which has passed through potassium dichromate solution, or a solution of the pigment itself, the mould remains colourless.

As regards the conditions of nutrition, proteid substances and peptone can serve as sources both of nitrogen and carbon. Tyrosine, asparagine, aspartic acid, leucine, nitrates, nitrites, ammonium salts, alanine, and glycine are also suitable nitrogenous nutrients. Urea, hippuric acid, creatine, and caffeine are unsuitable. The best carbonaceous foods are raffinose, starch, dextrin, maltose, and cellulose; dextrose, lævulose, mannose, and glycogen are less suitable; sucrose, galactose, lactose, arabinose, arabin, and inulin are still less favourable. Other carbon compounds which serve as food for the mould are glycerol, mannitol, erythritol, dulcitol, and in a slight degree ethyl alcohol, acetates, tartrates, lactates, and malates. Fats are not good sources of carbon but are utilised to some extent.

The suitability of a nitrogenous food depends on the nature of the carbonaceous food present, and *vice versa*. Comparing maltose, glucose, lactose, cane sugar, and glycerol, it was found that maltose is best in presence of tyrosine, glycine, hippuric acid, creatine, or leucine; sucrose is the best form of carbonaceous food when asparagine is present to supply nitrogen.

The mould grows in both acid and alkaline media.

Fats are slowly decomposed by *Monilia* into glycerol and fatty acids. Gelatin is liquefied by the mould both in alkaline and slightly acid condition. Starch, dextrin, sucrose, and maltose are hydrolysed, whilst lactose remains unchanged; cellulose is converted into a reducing sugar. The carbohydrates undergo still further changes, as the mould produces alcohol and various esters.

An enzyme, which the author terms *maltoglucose*, is exclusively and very unequally secreted when the mould is supplied with certain carbohydrates. It is not secreted when the carbonaceous food supplied is, for instance, glycerol; in glycerol, the amylolytic enzyme is found and this produces dextrose from starch. This shows that Duclaux's view is incorrect, namely, that when dextrose is produced by enzymes from starch, maltose is first formed, the maltose being converted by a second enzyme into dextrose. Maltoglucose is secreted in large quantities when raffinose, maltose, commercial dextrin, or starch is present; it is also secreted in presence of cellulose, galactose, xylose, and sucrose.

The secretion of maltoglucose is affected, not only by the nature, but by the amount of the food present. The author's results do not accord with the view that the secretion of enzymes generally is a result of the want of certain nutrients, and that it indicates a condition of hunger of the cell.

N. H. J. M.

Chemical Composition of the Pollen of the Sugar Beet. By ANTON STIFT (*Chem. Centr.*, 1901, i, 903—904; from *Oesterr. Zeit. Zuck. Ind. Landw.*, 30, 43—54).—The dry substance obtained from the pollen of the sugar beet was found to contain 3.6 per cent. of nitrogen, of which 2.6 was present as proteid nitrogen, 0.12 as ammonia, 0.4 as amino-acids and 0.14 as organic bases. Asparagine and glutamine could not, however, be detected. The ethereal extract (5.47 per cent.) probably contained very little fat, but considerable quantities of colouring matter and 1.57 per cent. of lecithin were

present. The composition of the pollen not only resembles that of animal semen in containing lecithin, but also in containing sodium chloride. 0.82 per cent. of starch and dextrin was also extracted from the pollen. Only a very small quantity of sucrose, however, was detected, but the pollen contained 0.52 per cent. of oxalic acid, present mainly as calcium oxalate with some alkali oxalate or free acid. Other organic acids are probably also present.

A comparison of the composition of this pollen with that derived from beet of different origin and locality shows considerable differences, especially in regard to the quantity of non-proteid nitrogen, ethereal extract, pentosans, and ash.

E. W. W.

Migration of Nitrogenous Substances and Ternary Substances in Annual Plants. By GUSTAVE ANDRÉ (*Compt. rend.*, 1901, 132, 1058—1060).—The plants selected were *Sinapis alba* as representing plants of rapid growth, with oily seeds, and *Lupinus albus*, which is of less rapid growth, and has highly nitrogenous seeds. Total nitrogen, amide nitrogen, fat, carbohydrates soluble in water (calculated as dextrose); saccharifiable carbohydrates (calculated as dextrose), and insoluble cellulose were determined in the seeds, in (1) the young plants and at the beginning of the flowering period (2), when the plants were in flower (3), and at the end of the flowering period (4).

In the case of *Sinapis*, the soluble nitrogen represented less than one-fourth of the total nitrogen in the first period, but increased to about one-third in the second period, being more abundant in the stems than in the roots. The absolute amount then diminished, but in the fourth period the soluble nitrogen represented 38 per cent. of the total for the whole plant, and about one-half of the total nitrogen of the fruit.

Similar results were obtained with lupins, which, however, contained high proportions of soluble nitrogen in the roots and stems, even during the period of maturation.

As regards ternary substances, it was found that whilst in *Sinapis* there was a decrease of soluble sugars in the roots, stems, and leaves during growth, there was a regular increase in the case of lupins.

N. H. J. M.

Migration of Ternary Substances in Annual Plants. By GUSTAVE ANDRÉ (*Compt. rend.*, 1901, 132, 1131—1134. Compare preceding abstract).—The roots of *Sinapis* contained nearly the maximum amount of saccharifiable carbohydrates (22.79 per cent.) at the beginning of the flowering period, the amount increasing to 25.74 per cent. at the end of this period; the percentage amounts in the stems were 14.69 and 26.27 respectively in the two periods. The insoluble cellulose in the stems increases less rapidly. In lupins, the saccharifiable carbohydrates remained almost the same (21—22 per cent.) in the stems, but increased in the roots and diminished in the leaves, and the amount in the leaves is much greater than in the case of *Sinapis*.

After extracting vegetable matter successively with light petroleum, dilute alcohol, hot dilute acid, treating with a cold mixture of sulphuric acid (53 c.c.), water (25 c.c.), and hydrochloric acid (23 c.c.), and then,

after dilution with water, boiling for 24 hours, a residue was obtained which contained C 60·28 and H 5·80 per cent. (Frémy's vasculose contains C 59·34 and H 5·49 per cent. ; Lange's lignin contains C = 59—61 per cent.). The substance is practically absent in seeds of *Sinapis*, and is present only in small amounts in the young plants, but the amount increases in all parts as the plants develop. In the portions where vasculose and saccharifiable carbohydrates occur in small amounts, proteids are abundant. It is probable that saccharifiable carbohydrates are chiefly utilised in the production of proteids, and not in forming vasculose.

N. H. J. M.

Quantity of Pentosans contained in Fruits and Vegetables. By CARL WITTMANN (*Chem. Centr.*, 1901, i, 959 ; from *Zeit. landw. Vers. Wes. Oest.*, 4, 131—139).—The quantity of pentosans contained in a large number of fruits, vegetables, fungi, &c., has been determined by Tollens and Krüger's modification of Counciler's method. The results are discussed and tabulated in the original paper. E. W. W.

Pentosans of Jute, Luffa, and Brewers' Grains. By. A. SCHÖNE and BERNHARD TOLLENS (*J. Landw.*, 1901, 49, 21—28).—Wheeler and Tollens (*Annalen*, 1889, 255, 327) obtained only about 0·7 per cent. of pure xylose from jute, whilst according to estimations by the authors, jute contains 17 per cent. of pentosans. Similarly, C. Schulze and Tollens (*Abstr.*, 1892, 1420) obtained only 1 per cent. of xylose from luffa, and about 5 per cent. from straw, the estimated amounts of pentosans in the latter substance being about 24—26 per cent.

The low yields of pentoses are partly due to decomposition during the process of heating with acid. Whilst the direct estimation of pentosans in jute showed a percentage of 12·70 of xylan, corresponding with 14·43 per cent. of xylose, determinations in the solutions obtained by heating jute at 100° with 3 per cent. sulphuric acid, and at 125—128° with 1 per cent. acid gave 10·35 and 10·97 respectively as the percentages of xylose. By extracting the wood gum from jute and converting it by Counciler's process (*Chem. Zeit.*, 1892, 1719) into xylose, 1·2 per cent. of xylose, $[a]_D + 19·2^\circ$, was obtained, whilst by heating the jute with 1 per cent. sulphuric acid at 125—128°, the yield was 0·95 per cent. By the latter method, luffa yielded 0·63 per cent. of pure xylose, $[a]_D + 17·9^\circ$.

Dry brewers' grains when heated on a water-bath with 3 per cent. sulphuric acid, yielded a solution which was found to contain 24·77 per cent. of pentosans (= 28·16 per cent. of pentoses). The solution contained 29·08 per cent. (of the grains) of reducing glucoses, which was only increased to 29·50 per cent. by heating with hydrochloric acid.

N. H. J. M.

A Reserve Carbohydrate, which produces Mannose, from the Bulb of *Lilium*. By J. PARKIN (*Proc. Camb. Phil. Soc.*, 1901, 11, 139—142).—The bulb-scales of the genus *Lilium* contain, in addition to starch, a reserve carbohydrate which exists as a sort of mucilage in the cell-sap of all the parenchymatous cells. It swells up and dissolves in water ; alcohol precipitates and hardens it, so that

sections of scales preserved in spirit show each cell filled with a solid block of mucilage, in which the starch grains are imbedded. It was obtained, by extraction with cold water and precipitation with strong alcohol, as a translucent, almost colourless, tough solid; it gives no marked colour with iodine; it appears to be dextrorotatory. When it is hydrolysed with 2 per cent. sulphuric acid, it yields a sugar which was identified as mannose by means of its cupric reducing power, rotation, and its phenylhydrazone; the original carbohydrate may be identical with the mannan of previous observers. It was obtained from *Lilium candidum* and *L. auratum*; probably the same carbohydrate exists also in *L. bulbiferum*, *L. croceum*, *L. dauricum*, *L. lancifolium*, *L. longiflorum*, and *L. Martagon*. C. F. B.

Proteids of Seeds. By THOMAS BOKORNY (*Bied. Centr.*, 1901, 30, 261—263; from *Bot. Centr.*, 1900, 82, 289—306).—The proteids soluble in 5—10 per cent. salt solutions are stored in the protein grains and albumin crystals; proteid insoluble in sodium chloride solutions was not usually found in protein grains. Fat was never detected in protein grains and is probably uniformly mixed with the plasmatic albumin. Active proteid could not be detected in protein grains. The whole of the proteid residue of the seed tissues, after extracting the protein grains, dissolves in aqueous potash. The gluten substances of cereals dissolve in cold or hot 70—80 per cent. alcohol, a solution used in other cases for precipitating proteids.

Peptones could not be detected in resting seeds. Propeptone (albumose) was sometimes found in traces, and may have been produced by the boiling in presence of acetic acid.

Asparagine, tyrosine, and leucine, which are widely distributed in seeds, seem to be the last intermediate products in the formation of proteids as well as the first decomposition products. N. H. J. M.

Voandzia Subterranea. By BALLAND (*Compt. rend.*, 1901, 132, 1061—1062).—*Voandzia subterranea* (glycine or haricot pistache) is a widely distributed, leguminous plant cultivated by negroes in the intertropical portions of Africa. The fruit is a pod with seed which ripens in the soil like the earth-nut. The seeds have the following percentage composition:

| Water. | Nitrogenous matter. | Fat. | Starchy matter. | Cellulose. | Ash. |
|--------|---------------------|------|-----------------|------------|------|
| 9.80 | 18.60 | 6.00 | 58.30 | 4.00 | 3.30 |

On the assumption that the human organism requires daily 120—130 grams of nitrogenous matter, 56 grams of fat, and 500 grams of carbohydrate, it will be seen that, allowing for coefficients of digestibility, 1 kilogram of the seeds will supply the amounts required of the different forms of food. N. H. J. M.

Sugar as Food for Cattle. By FRANZ LEHMANN (*Bied. Centr.*, 1901, 30, 178—181; from *Hannov. Land. Forstwirt. Zeit.*, 52, No. 48).—In 1885, Lawes and Gilbert showed that for fattening pigs, sugar is equivalent to starch. The results of experiments with sheep made at Göttingen in 1885 gave less satisfactory results; 100 kilos. of sugar were found to correspond with only 82.1 and 88.1 kilos. of carbo-

hydrates in ordinary fattening foods (compare Maercker, *Abstr.*, 1885, 1149, and Henneberg, *ibid.*, 1252). In experiments with bullocks, Holdefleiss obtained an increase of 0.315 kilo. per 1 kilo. of sugar. Maercker's experiments with pigs showed a gain of 0.7 kilo. per kilo. of sugar.

In experiments at Göttingen, 980.5 kilos. of sugar (third product) were fed, resulting in a gain of 317.1 kilos. of live weight. The results are not considered altogether satisfactory, because the rations employed were not the most suitable. It is thought that if, for instance, crushed grain, potatoes, maize, and dairy refuse, &c., had been employed, less satisfactory results for sugar would have been obtained.

Feeding with sugar does not improve the quality of meat. Albert's experiments on this point are open to criticism, otherwise his results would have to be considered unfavourable rather than favourable to the employment of sugar.

N. H. J. M.

Pig Feeding Experiments with Molasses, Peat Molasses and Palm-kernel Molasses at Proskau. By J. KLEIN (*Bied. Centr.*, 1901, 30, 280; from *Milchzeit.*, 1899, No. 12, 13).—Grain (1 kilo.) is equivalent to molasses, or peat molasses (1.25 kilos.), with meat meal (0.125 kilo.); or to palm-kernel molasses (1.21 kilos.) without meat meal. Considerable amounts of molasses may be given if the amount is gradually increased. With pigs 3½ to 8 months old the amount can be increased from 150 to 1275 grams per day, or, in the case of palm-kernel molasses, to 1200 grams. Peat molasses seems to be the best form.

N. H. J. M.

Pig Feeding Experiments with Sugar and Palm-kernel Seed at Proskau. By J. KLEIN (*Bied. Centr.*, 1901, 30, 283; from *Milchzeit.*, 1900, No. 20, 21).—In addition to maize and moderate amounts of milk and whey, the pigs received sugar and palm cake, and palm cake alone respectively. The food did not agree with the pigs, but the results showed that sugar had a distinct effect on the nature of the fat produced.

In a second series of experiments, the milk and whey were omitted, the pigs receiving instead a corresponding amount of meat meal. The results showed that sugar was favourable to fat production. The iodine numbers of the fat were considerably higher in the second series of experiments than in the first.

N. H. J. M.

Chlorine Requirement of Buckwheat. By ADOLF MAYER (*J. Landw.*, 1901, 49, 41—60).—The experiments were instituted owing to very unsatisfactory results obtained when buckwheat had been manured with kainite. In opposition to Nobbe (*Landw. Versuchs-Stat.*, 6, 118, and 13, 398), it is maintained that chlorine is practically of no importance in the cultivation of buckwheat, and that even moderate amounts of potassium salts, which, like the modern so-called kainite, contain several equivalents of chlorine to one of potassium, may cause great injury to the crop.

N. H. J. M.

Plot Experiments at Jersitz-Posen in 1898—1899 and 1899—1900. By MAX GERLACH (*Bied. Centr.*, 1901, 30, 236—238; from *Jahresber. Landw. Versuchs-Stat. Jersitz-Posen*, 1898—1899, p. 44, and

1899—1900, p. 21).—The soil of the plots, which are mostly 160 square metres, contains N, 0.110 ; K_2O , 0.102 ; CaO , 0.710, and P_2O_5 , 0.1555 per cent.

With barley, nitrogenous manure produced a decided increase, and nitrogen as ammonia gave nearly the same increase as nitrate. The percentage of nitrogen was in each case high for brewing barley, but the grain was considered to be good for brewing. In the case of oats, phosphatic manure produced very little effect. In 1898, owing to the dry weather, kainite had very little effect on sugar beet ; but there was no depression in the percentage of sugar even when 8 cwt. was applied.

Nitrogen in the form of ammonia produced no after effect, in the second year, the yield being less than when no ammonia had been applied. There was a slight apparent after effect in the case of nitrate, but this is attributed to inequality in the treatment of the land.

Autumn manuring with ammonium salt had no effect on rye, whilst spring manuring with nitrate increased the yield. N. H. J. M.

Inoculation of the Soil with Alinit. By L. MALPEAUX (*Ann. Agron.*, 1901, 27, 191—206. Compare *Abstr.*, 1900, ii, 498).—Pot and field experiments with oats, maize, and white mustard are described. The results accord with the earlier ones indicating that alinit only acts in soil rich in organic matter by rendering available the insoluble nitrogenous substances present. Consistent results were obtained in the pot experiments, but on a larger scale the results are conflicting, and the conclusion is drawn that alinit has no favourable effect on ordinary arable soil. N. H. J. M.

Estimation of the Manurial Requirements of Typical Soils. By MAX GERLACH (*Bied. Centr.*, 1901, 30, 234—236 ; from *Jahresber. Landw. Versuchs-Stat. Jersitz-Posen*, 1898—1899, p. 30).—Pot experiments were made in which barley, followed by white mustard, was grown in six different soils, containing N, 0.030 to 0.257, and P_2O_5 , 0.012 to 0.173 per cent. The results showed that the amount of available nitrogen was in every case so small that nitrogenous manures were necessary for the first crop. As regards phosphoric acid, only one of the soils was much benefited by phosphatic manure for the first crop ; all six soils required phosphoric acid for the second crop. N. H. J. M.

Conditions of Soil and Water in the Province Rheinhessen in the Rheingau and Taunus. By C. LUEDECKE (*Bied. Centr.*, 1901, 30, 145—168 ; from *Mitt. Landw. Inst. K. Univ. Breslau*, 1899, Heft 2, 45).—Analyses were made of 500 samples of soil and subsoil obtained from different geological layers. Besides determinations of calcium (and in some cases magnesium and carbon dioxide), complete analyses were made of extracts by hot dilute hydrochloric acid. Mechanical separations were made, and the water-holding capacity of the soils was determined. The results are given in numerous tables.

In determining calcium and magnesium, the soil (2—25 grams) was heated at 70° with twice the amount of 10 per cent. hydrochloric acid.

The extracts for determining the total soluble constituents were

prepared by treating the soil (25—50 grams), previously dried at 110° , with sufficient 10 per cent. hydrochloric acid to decompose the carbonates. The soil is then heated on a water-bath with acid of the same strength (twice the weight of the soil). The filtered extract is evaporated to dryness with nitric acid. The different methods employed for the different constituents are those described by Bieler and Schneidewind.

The absorption coefficient for nitrogen was determined in 50 grams of soil which passes through 0.5 mm. sieves (round holes) with 100 c.c. of a solution of ammonium chloride containing 1 c.c. of nitrogen per c.c. The results are calculated so as to show how much nitrogen (in c.c.) at a pressure of 760 mm. at 0° is absorbed by 100 grams of soil from 200 c.c. of solution.

The results of a large number of analyses of river and well waters of the same districts are given in tables. N. H. J. M.

Soil of the Experimental Field of the Royal University of Bremen at Rosenthal. By KURT VON RUMKER and H. HOFFMAN (*Bied. Centr.*, 1901, 30, 220—224; from *Mitt. Landw. Inst. K. Univ. Breslau*, 1900, Heft 3, 1).—Mechanical analyses of 85 soil samples were made. The chemical analyses were made by Wohltmann's methods (*Abstr.*, 1897, ii, 463), with some modification. Addition of sodium chloride in evaporating the hydrochloric acid extract was found to be unnecessary.

The results of soil analyses are given in tables. The treatment of the field from 1893—1894 to 1897—1898 is described in the original paper. N. H. J. M.

Losses of Nitrogen in Fresh Cow Urine and Cow Dung kept in Thin Layers, Alone and with Straw. By KRENZ and MAX GERLACH (*Bied. Centr.*, 1901, 30, 232—234; from *Jahresber. Landw. Versuchs-Stat. Jersitz-Posen*, 1898—1899, p. 26).—Fresh cow fæces kept at 16° on flat plates, alone and with straw, did not lose more than 3.1 per cent. of nitrogen in 10 days. In the case of urine, the greatest loss was 3.5 per cent. in 3 days, and 14.8 per cent. in 5 days. The results of similar experiments with a mixture of fæces and urine showed a loss of 0.9 per cent. of nitrogen in 24 hours; in 3, 5, and 10 days, however, the losses of nitrogen were 11.6, 12.1, and 18.9 per cent. respectively. In presence of straw, the losses of nitrogen in the mixed excrement were slight in the first 24 hours, and amounted to 20.6 per cent. in 10 days.

It was found that when fresh excrement is added to older dung, the production of ammonium carbonate is not quickened as might be expected; the loss of nitrogen in 24 hours was 0.8 per cent., and in 3 days 4.0 per cent. N. H. J. M.

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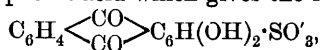
Classification of Acid and Alkali Indicators. By JULIUS WAGNER (*Zeit. anorg. Chem.*, 1901, 27, 138—151).—The author condemns the classification suggested by Glaser (*Abstr.*, 1899, ii, 572) as having no chemical basis and founded only on practical efficiency. A better system is formed when the indicators are classified according to the kinds of ions which they give. Two classes are recognised, each with two sub-groups: A. Indicators with a characteristic univalent ion: (i) with characteristic univalent anion, (ii) with characteristic univalent cation. B. Indicators with polyvalent ion: (i) with positive and negative ion (amphoteric electrolyte), (ii) with uni- and bi-valent anion or cation.

To class A (i) belong amongst others the indicators, iodo eosin, cochineal, fluorescein, alizarin, *p*-nitrophenol, rosolic acid, lacmoid, litmus, and phenolphthalein. The weaker the acid of the indicator the more sensitive is the colour change; but as in this case the degree of hydrolysis is high, the indicator may only be used with strong bases. For the titration of weak bases one of the stronger acid indicators must be employed. The order given is the order of the strengths of the acids contained in the indicator.

Only two indicators are known belonging to class A (ii), namely, methyl-violet and dimethylaminobenzene.

The indicators of class B (i) give different colours in acid and alkaline solution. The substances included in this group are: Tropæolin OO, methyl-orange, ethyl-orange, Congo-red, and benzopurpurin. The action of methyl-orange is discussed at some length and exception is taken to Küster's (*Abstr.*, 1897, ii, 74) interpretation of the intermediate tint obtained with this indicator when the solution contains free carbon dioxide. The explanation offered for this tint is that the acid of methyl-orange is itself reddish; when carbon dioxide is passed into a solution of it, some undissociated acid is formed, and the colour of this along with the yellow of the anion gives the observed tint, which is not a mixture of the red of the cation with the yellow of the anion. (On the ions of methyl-orange, see Bredig and Winkelbach, *Zeit. Elektrochem.*, 1900, 6, 35). A similar explanation is applicable to Congo-red. The sensitiveness of the indicators of this class depends in a large measure on the difference of the colours of the anion and of the cation, and an intermediate tint is always obtained when the undissociated substance is coloured.

In the last class we have those indicators which give differently coloured ions of the same kind. So far only acids of this type are known. Alizarinsulphonic acid which gives the red ion,



and with more alkali the violet ion, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}(\text{OH}) \begin{array}{c} \diagup \text{SO}'_3 \\ \diagdown \text{O}^3 \end{array}$, belongs to this class. Indicators of this type would be useful for

determining phosphoric acid in presence of phosphates, or a weak acid in presence of a strong acid, but no entirely satisfactory one is yet known. J. McC.

Modification of the Manganimetric Method. By J. GAILHAT (*Bull. Soc. Chim.*, 1901, [iii], 25, 395—402).—Volumetric processes involving the use of potassium permanganate are inapplicable in the case of substances undergoing oxidation only at the boiling temperature in acid solution. Under such conditions, the permanganate is itself decomposed, the loss of oxygen being a function of the acidity and of the concentration. A large number of experiments are recorded which show that in the presence of an excess of manganese sulphate (that is, of a quantity containing twice as much manganese as the permanganate employed) and of not more than 20 per cent. by volume of sulphuric acid, the loss of oxygen is practically constant for a time of ebullition ranging from 5 minutes to an hour. Accurate results have thus been obtained in the estimation of glycerol, the substance being boiled with a definite volume of potassium permanganate solution in the presence of sulphuric acid and manganese sulphate, the liquid subsequently titrated with standard oxalic acid, and the result compared with that obtained in a blank experiment carried out under similar conditions. N. L.

New Calcium Chloride Apparatus. By G. F. HENNING (*Zeit. anal. Chem.*, 1901, 40, 168).—This pattern is in the form of an ordinary narrow-necked bottle with two side tubes, that for the entry of the gas being continued inside to the bottom of the bottle, and expanded outside into a bulb. The neck can be closed either by fusion or by a stopper after filling. The apparatus does not require to be suspended, but stands on the balance pan. M. J. S.

Estimation of Ozone. By ALBERT LADENBURG and REINHOLD QUASIG (*Ber.*, 1901, 34, 1184—1188. Compare this vol., ii, 232).—The direct estimation of ozone by weighing affords a check on the methods of estimating this substance volumetrically. By comparing the results obtained gravimetrically with those obtained by absorption in potassium iodide, and subsequent titration of the liberated iodine, it has been found that correct results are only obtained when the gas is passed into neutral potassium iodide solution. The solution is then acidified and titrated with sodium thiosulphate. In this way, the end reaction is quite sharp, and no subsequent liberation of iodine occurs. On the other hand, when the ozone is absorbed by acid potassium iodide solution, the end of the reaction is not sharp, and the amount of ozone found is considerably too high. The reason for this has not been definitely ascertained, but it is possibly owing to the occurrence of the reaction $4\text{O}_3 + 10\text{HI} + \text{H}_2\text{O} = 5\text{I}_2 + \text{H}_2\text{O}_2 + 5\text{H}_2\text{O} + 3\text{O}_2$. A. H.

Estimation of Sulphur in Wrought Iron and Steel. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1901, 23, 147—151).—The methods for the estimation of very small quantities of sulphur in steel are still somewhat defective, as the result differ considerably in the third, and often in the second, decimal place according to the process used.

When using the evolution method, the author is now in the habit of adding one-fourth to the amount of sulphur found; thus for instance, 0.012 found is held to indicate the presence of 0.015 per cent.

L. DE K.

Loss of Sulphur in Preparing Ash of Plants. By GEORGE S. FRAPS (*J. Amer. Chem. Soc.*, 1901, 23, 199—200).—Of each of nine different plants, 10 grams were burnt to ash at the lowest possible temperature, and another 10 grams were burnt after addition of 20 c.c. of a solution of calcium acetate containing 29.2 grams of the salt per litre (Shuttleworth's process). Whether the calcium acetate retains all the sulphur or not is still questionable, but when no such addition was made, the loss in sulphur amounted to 4, 28, 6, 100, 16, 11, 68, 58, and 58 per cent. of that found when calcium acetate was used.

L. DE K.

Estimation of Hydrogen Sulphide in Illuminating Gas. By C. C. TUTWILLER (*J. Amer. Chem. Soc.*, 1901, 23, 173—177).—The apparatus consists essentially of a burette provided at the top and bottom with three-way stopcocks and communicating at the top through one of the outlets with a 10 c.c. glass-stoppered cylinder graduated to 0.1 c.c. The enlarged part of the burette holds 100 c.c., and its stem has two graduations, one at the 100 c.c. mark and the other at 50 mm. from the bottom stopcock, dividing the remaining space into two divisions of 5 and 10 c.c. respectively. A mercury level bulb may be connected with the stopcock below.

The stopcocks being made to communicate with the interior of the burette, the gas to be tested, freed from tar if necessary by filtration through cotton, is passed through the burette for a few minutes to displace the air. After closing the burette and waiting for a few minutes, the gas is compressed by raising a mercury reservoir attached to the bottom stopcock until the mercurial column reaches the 100 c.c. mark; by momentarily opening the top, the excess of gas escapes, and exactly 100 c.c. at the ordinary pressure are left. By closing the top, opening the bottom stopcock, and lowering the mercury, the gas is obtained under a reduced pressure, 5 c.c. of starch water very faintly coloured with iodine are introduced, and a standard solution of iodine is added 3 or 4 drops at the time, well shaking after each addition until the starch water assumes a permanent bluish colour. If the solution contains 0.0017076 gram of iodine per c.c., then each c.c. will be equivalent to 100 grains of hydrogen sulphide per 100 cubic feet of gas.

L. DE K.

Detection of Selenium in Sulphuric Acid. By ADOLPHE JOUVE (*Bull. Soc. Chim.*, 1901, [iii], 25, 489—491).—Among the tests for the presence of selenium in sulphuric acid, two are comparatively delicate. The one, based on the production of a blue coloration with codeine (and equally well, it is stated, with morphine), is capable of detecting at most 1 part of selenium in 200, whilst the second, consisting in the precipitation of red selenium by passing a current of sulphur dioxide into the diluted acid, may attain a delicacy of 1 in 10,000. If the selenium is present as selenic acid instead of selenious acid, the

first test is inapplicable, and the second is obtained with difficulty. The use of a current of acetylene as a reducing agent affords a still more delicate test, capable of detecting 1 in 100,000 of selenium; the red coloration is more rapidly produced if the gas contains hydrogen chloride. N. L.

Estimation of Nitrates in Water by means of Stannous Chloride. By H. HENRIET (*Compt. rend.*, 1901, 132, 966—968. Compare Divers and Haga, *Trans.*, 1885, 623).—The reduction of nitric acid to hydroxylamine by the action of stannous chloride takes place quantitatively when the solution is rendered strongly acid with hydrochloric acid. The residue, obtained by evaporating to dryness 50 c.c. of water, is boiled for 10 minutes with a known excess of stannous chloride and dissolved in concentrated hydrochloric acid; the solution is then titrated with standard iodine solution, the amount of stannous chloride which has disappeared being a measure of the nitrogen present. In this estimation, 6 atoms of iodine correspond with 1 of nitrogen. Organic matter does not interfere with the reaction, but iron salts must be removed by treating the water with ammonia before evaporation. G. T. M.

Nitrites in Milk. By H. WEFERS BETTINK (*Chem. Centr.*, 1901, i, 854; from *Ned. Tijdschr. Pharm.*, 1901, 13, 67).—Most of the usual tests for nitrites fail when applied to milk; the most delicate is Riegler's, which consists in adding to 10 c.c. of the liquid, 50 mg. of a mixture of equal parts of 1:4-naphthylaminesulphonic acid, and β -naphthol, and then 6 drops of strong hydrochloric acid, and, after shaking for a minute, adding 1.5—2 c.c. of ammonia. Nitrites produce a strong, yellowish-red coloration. Milk should first be coagulated with a few drops of hydrochloric acid, and the filtrate employed. Should a doubt remain whether a feeble colour produced is due to a nitrite, the mixture is filtered, and the precipitate dissolved from the filter by strong alcohol, which will dissolve the red colouring matter, but in the absence of nitrites will at most become feebly yellowish.

M. J. S.

Estimation of the Nitroso-groups in Organic Compounds. By ROBERT CLAUSER (*Ber.*, 1901, 34, 889—895).—Compounds containing a nitroso-group react with phenylhydrazine (1 mol.) forming benzene, water, nitrogen (1 mol.), and (generally) an azo-compound. Directions are given by which the quantitative estimation of the nitroso-groups in a compound can be made by measuring the amount of nitrogen evolved in the reaction with phenylhydrazine. Before measuring the nitrogen, it is completely saturated with benzene, corrections then being made for the tension of the benzene and aqueous vapours. R. H. P.

Phosphorised Oil. By KONRAD STICH (*Chem. Centr.* 1901, i, 796—797; from *Wien. klin. Woch.*, 14, 177).—Mitscherlich's method will detect 0.0002 per cent. of phosphorus in phosphorised oils if air is occasionally admitted to the distillation tube. M. J. S.

Estimation of Free Phosphorus in Phosphorised Oils. By ADOLF FRÄNKEL (*Chem. Centr.*, 1901, i, 912; from *Pharm. Post.*, 1901, 34, 117).—Mitscherlich's method, with the modifications of Scherer, and of Nattermann and Hilger (*Abstr.*, 1898, ii, 453) although excellent as a qualitative test, has given in the author's hands only 41 per cent. of the phosphorus taken. The method of Louise (*Abstr.*, 1899, ii, 807) is regarded as inaccurate, since reduction of silver would be produced by the aldehyde in the acetone, by phosphorous acid, and even by certain constituents of cod-liver oil itself. It has also been shown by Nattermann and Hilger that silver phosphide is decomposed by water into silver and phosphorous acid, which latter would escape estimation. The author therefore dissolves the substance in ether, precipitates with a hot alcoholic solution of silver nitrate, oxidises the dried precipitate with aqua regia and estimates the phosphorus as phosphoric acid. Applied to a solution in bitter-almond oil, this method yielded 84—90 per cent. of the phosphorus taken. There is always a loss of phosphorus when preparing solutions of that substance in oils, and a still further loss takes place on keeping. Statements to the contrary by Jolles and Kassowitz were probably based on the above erroneous methods of estimation. M. J. S.

The Effect on the Marsh Test of some Commercial Products containing Selenium and Tellurium. By ALBERT E. BERRY (*J. Soc. Chem. Ind.*, 1901, 20, 322—324).—The mirrors obtained when testing for arsenic in the Marsh apparatus may be totally or partially due to the presence of selenium and possibly of tellurium. To guard against errors, the author suggests the following method. The tubes are treated first with a hot solution of potassium cyanide which dissolves any selenium or sulphur present and leaves the arsenic and any tellurium practically undissolved. On treating the residue with solution of calcium hypochlorite, the arsenic is dissolved leaving any tellurium which can then be fused and further identified. The author has not, as yet, met with tellurium in any commercial products but has frequently met with selenium. L. DE K.

Use of Metallic Sodium in Blow-pipe Analysis. By CHARLES LATHROP PARSONS (*J. Amer. Chem. Soc.*, 1901, 23, 159—161).—A modification of Hempel's method. A piece of sodium, 3 or 4 mm. in diameter, is hammered out flat on a smooth surface, the powdered substance to be tested is spread upon it, pressed into the metal with the hammer and the whole kneaded into a little ball with a knife blade. It is then placed upon a slight depression in a piece of charcoal and ignited with a match or the Bunsen flame. The reduction takes place instantaneously. The residue is now heated before the blowpipe, and as the sodium compounds melt and are absorbed by the charcoal, the fusible metallic particles collect readily into a button and may then be recognised by their behaviour.

The process may be successfully applied to minerals such as galena, cassiterite, chrysocolla, &c. L. DE K.

Quantitative Analysis of Lithiniferous Waters; Comparison of the Spectroscopic with the more Common Methods. By G. RANZOLI (*Gazzetta*, 1901, 31, i, 40—48).—A description of the

various gravimetric methods of estimating lithium in mineral waters is given, and is followed by a discussion of Ballmann's spectroscopic method with the modifications introduced into it by Föhr and by Nasini and Anderlini. Comparative experiments show that the method of the last-named authors gives far more accurate results than any of the gravimetric methods or Föhr's original method.

T. H. P.

Precipitation of Certain Metallic Sulphides with Sodium Thiosulphate. By EDUARD DONATH (*Zeit. anal. Chem.*, 1901, 40, 141—143).—A cadmium or nickel solution (chloride or sulphate) supersaturated with ammonia and then mixed with excess of acetic acid, gives, on boiling for half an hour after addition of powdered sodium thiosulphate, a precipitate containing all the cadmium or nickel, mixed with sulphur. A solution of zinc, cobalt, iron, or manganese, in similar circumstances, gives a sulphur precipitate containing only traces of the metal. The method cannot, however, be employed for quantitative separation since part of the zinc, cobalt, manganese, or iron is always carried down by the other metal. The method can very well be employed for detecting traces of nickel in presence of much cobalt.

M. J. S.

Influence of Pyrites and other Sulphides on the Estimation of Bivalent Iron. By WILLIAM F. HILLEBRAND and HENRY N. STOKES (*Zeit. anorg. Chem.*, 1901, 27, 125—126. Compare Abstr., 1900, ii, 763, and this vol., ii, 284).—An admission of de Koninck's claim for priority (*Ann. Soc. geol. Belg.*, 1882—1883, 10, 101).

J. McC.

Potassium Thiocyanate as Indicator in the Reduction of Ferric to Ferrous Salts. By A. EBELING (*Zeit. öffentl. Chem.*, 1901, 8, 144—145).—The solution containing the ferric salt is mixed with 1 to 2 drops of solution of potassium thiocyanate (1 : 10) which causes a deep red coloration. Dilute sulphuric acid and zinc are added, and as soon as the colour has disappeared showing the complete reduction of the ferric iron, the liquid is titrated, as usual, with standard permanganate.

L. DE K.

Electrolytic Estimation of Bismuth. By KARL WIMMENAUER (*Zeit. anorg. Chem.*, 1901, 27, 1—21).—The author has examined the methods for the electrolytic estimation of bismuth and gives details of his results. An accurate and expeditious estimation is best obtained as follows.

The electrolyte should contain 0.1 gram of bismuth oxide to 1—0.5 c.c. of concentrated nitric acid and if an excess of nitric acid is not employed 2—4 c.c. of glycerol (1 part glycerol to 2 parts water) must be added, and the solution diluted to 150 c.c. When this solution is subjected to electrolysis, using a current of 0.1 ampere at first, and reducing this to 0.05 ampere as soon as any indication of peroxide is detected, a dense, bright deposit is obtained, which is easily washed without loss. It is essential that the electrolyte should be continuously agitated during the deposition. Quantities up to 0.4 gram of bismuth are easily deposited in 3 hours. The temperature of

the solution is gradually raised to 50° and maintained at this until all the bismuth is deposited. The results are within 0.1 to 0.25 per cent. of the theoretical.

E. C. R.

Estimation of the Hardness of Water. By MAX PLEISSNER (*Chem. Centr.*, 1901, i, 796; from *Pharm. Centr. Halle.*, 1901, 42, 145—147).—In estimating the hardness of water by Faisst and Knauss' modification of Clark's method, it is recommended to use a concentrated soap solution, so that in titrating 100 c.c. of water, 1 c.c. shall correspond with 1° (German) of hardness. Such a solution is obtained by dissolving 20 grams of Marseilles soap in dilute alcohol to 1 litre: 100 c.c. of it should be required to give a permanent (5 minutes) lather with 100 c.c. of barium chloride solution containing 0.0436 gram of crystallised barium chloride; 100 c.c. of distilled water require 0.25 c.c. of this soap solution to give a lather. The hardness (x) in German degrees is calculated from the number of c.c. (n) by the formula $x = (10n - 10)/9$. Turbid waters should be filtered; those of more than 20° hardness, diluted. If magnesium is present the 5 minute limit should be adhered to strictly. Organic substances and alumina interfere with the result.

M. J. S.

Detection of Alcohol in Milk. By UHL and OTTO HENZOLD (*Chem. Centr.*, 1901, i, 973; from *Milch. Zeit.*, 1901, 30, 181).—On the evidence of the iodoform test, it has been stated that alcohol has been found in milk. A milk distillate which gave the iodoform reaction could not be made to yield ethyl acetate, and, therefore, probably contained an aldehyde derived from the distillation of lactic acid. Aldehydes have been unmistakably obtained from the distillate of milk in which a pure lactic acid fermentation had been established. The proteids of milk also, on distillation with water, yield products which give the iodoform reaction. This reaction cannot therefore be accepted as a proof of the presence of alcohol in milk.

M. J. S.

Characteristic Reaction of Phenol. By PAOLO FIORA (*Chem. Centr.*, 1901, i, 843; from *Boll. Chim. Farm.*, 1901, 40, 76).—With peppermint oil, phenol gives a substance of a greenish-blue colour, apparently of the composition $C_6H_5O \cdot CH_2 \cdot C_9H_{17}$, resulting from condensation of phenol with menthol. The colour is not produced by guaiacol, resorcinol, or by creosote. It disappears on heating, but returns with full intensity on cooling if the phenol is in excess, otherwise somewhat more feebly. The reaction is not produced by sodium phenoxide, and it has not hitherto been found possible to employ it for detecting phenol in creosote or in guaiacol.

M. J. S.

Positive Indications with the Phenylhydrazine Test in the Absence of Sugar. By ADOLF JOLLES (*Chem. Centr.*, 1901, i, 915; from *Pharm. Post.*, 1901, 34, 120).—Crystals which in appearance and melting point resemble glucosazone are obtainable from urine which contains condensed glycuronic acids or nucleoalbumins. After the removal of these by precipitating with magnesium sulphate, both the phenylhydrazine and the fermentation tests gave negative results.

Albuminous urines often appear to give the phenylhydrazine reaction, although containing no fermentable constituent. Albumin should therefore be separated before applying the phenylhydrazine test.

M. J. S.

A New Sensitive Test for Sugar. By E. RIEGLER (*Chem. Centr.*, 1901, i, 799; from *Deut. med. Woch.*, 1901, 27, 40).—About 1 c.c. of urine is mixed with 0.1 gram of phenylhydrazine hydrochloride, 0.5 gram of sodium acetate, and about 2 c.c. of water, and heated to boiling; 10 c.c. of 10 per cent. sodium hydroxide is immediately added and the mixture shaken. If 0.1 per cent. of sugar is present, the mixture will acquire a reddish-violet colour in about 5 minutes, or in 1 minute if the operation is performed in a basin. Other aldehydes give a similar reaction.

M. J. S.

Scheibler's Extraction Method for the Determination of the Polarisation of Beets. By ALEXANDER HERZFELD (*Zeit. Ver. deut. Zuckerind.*, 1901, 334—335).—The author describes this method as carried out in the laboratory of the Verein der deutschen Zucker-Industrie. In the extraction apparatus employed, the flask consists of two bulbs each holding about 100 c.c. and connected by a short tube about 1 cm. in width, on which is the 100 c.c. (at 20°/4°) mark of the lower bulb. The extractor is that of Müller and allows of a sample of the liquid being removed by means of the stoppered side tube. A short glass Soxhlet's condenser is used. The process is carried out as follows: 26 grams of the beet pulp are weighed out in a nickel basin and well mixed therein with 3 c.c. of lead acetate solution and a few c.c. of 90 per cent. alcohol. The mass is then washed by means of 90 per cent. alcohol into the extractor, the inside end of the siphon tube being covered with a circular piece of wire gauze about 3 cm. in diameter. The pulp is then distributed uniformly in the lower part of the extractor by means of a glass rod which is finally washed with alcohol. The quantity of alcohol taken must be such that the lower bulb is about 3/4 full when all the liquid has passed down by the siphon. After being connected with the condenser, the apparatus is arranged in a rather deep water-bath, so that the alcohol can be kept briskly boiling, the liquid being siphoned off from the pulp at least every 5 minutes and where possible every 3 or 4 minutes. After about 2 hours' extraction, a sample of the liquid is removed from the siphon tube and tested for sugar by the α -naphthol and sulphuric acid test, the extraction being continued until no coloured ring is obtained. When this is the case, the apparatus is disconnected, the contents of the flask are cooled to 20°, made up to the mark with 90 per cent. alcohol, filtered, and the polarisation read off in the ordinary way.

T. H. P.

Evaluation of Gum Arabic. By OTTO FROMM (*Zeit. anal. Chem.*, 1901, 40, 143—168).—The object of this investigation was to obtain comparative values for the adhesive strength of different samples of commercial gum arabic, and to ascertain what connection, if any, existed between the adhesive strength and other properties of the substance which could be ascertained with rapidity and accuracy. Since

it appears from the researches of Dalén (*Mitt. K. tech. Versuchsanstalt*, 1894, 149) that the relative adhesive strength of different samples is not constant with different strengths of solution, all the experiments were made with solutions of the same sp. gr. (1.035 at 15°/15°), which corresponds with 8.5 per cent. of dry, or 10 per cent. of air-dry, gum. The solutions were filtered through cotton wool, and the opportunity taken of observing their colour and tendency to froth, as well as the bulk of the slimy and other insoluble substances. The proportion of slimy matter seems to have an important connection with the so-called "ripeness" of the gum; the comparative amount was estimated by rinsing it from the filter into a graduated cylinder and reading the bulk after subsidence for one night. The viscosity of the solution was estimated with an Engler's viscosimeter at 20°, and compared with water of the same temperature. The value approximates to 2, wide deviations from that number being rare. The acidity is easily estimated by titration with *N*/10 alkali, using phenolphthalein as indicator. The acidity of the solution increases on keeping, both in closed and open vessels, rising more than 50 per cent. in less than a month; the viscosity during the same time undergoes a quite inconsiderable diminution. The optical rotation of the solution was measured in a 1 dm. tube. Most of the samples showed negative rotation, the value α_D lying between -2° and -3° , but a few gave dextrorotation, and a considerable number were almost inactive. Reducing substances were always present, but the amount was small and showed no connection with the optical behaviour. With few exceptions, the solutions gave a thick precipitate with lead acetate.

The direct estimation of the adhesive strength was carried out by the method of Dalén, which consists in saturating porous paper with the gum solution, drying, and ascertaining the increase in the resistance to a rending strain by means of a Schopper apparatus. Numerous precautions are essential, an important one being that the strip of paper must be dried in air which is 65 per cent. saturated with moisture. A special drying chamber was devised for this purpose. The method of stating the results was that which is now usually adopted for expressing the strength of paper itself, namely, the length of the strip of paper which would cause fracture by its own weight, the absorbed gum being regarded as though it formed a separate film of the area of the paper employed. The mean increase in the breaking load recorded by the testing machine was therefore multiplied into the length of the strip of paper (18 cm. \times 15 mm.) and divided by the weight of dry gum absorbed. Values up to 15 kilometres were obtained.

A comparison of all the results showed that gums of high adhesive strength exhibited high viscosity of solution, high acidity, and high levorotation, and that a considerable deviation from the mean value in any one of these factors is always connected with inferiority in adhesive strength. The following limits are laid down. The solution of specific gravity 1.035 should have a viscosity of at least 2 at 20°; in a 1 dm. tube, it should show negative rotation of at least $2^\circ 30'$; 50 c.c. of the solution must require for neutralisation at least 2.1 c.c. of *N*/10 alkali; it must be precipitated by lead acetate, and reduce

only a small amount of copper solution; its breaking length will then exceed 14 kilometres, and its elongation at breaking strain 2 per cent.

The interesting question is raised how far gum arabic retains these properties on keeping. In some cases, no change could be detected after 5 weeks, but in other cases a distinct deterioration in adhesive strength, accompanied by diminished viscosity and acidity, with increase in the insoluble slimy substances, was observed in that time. This subject will be followed up further. M. J. S.

New Method of Detecting Acetic Acid in Urine. By S. LIPLIAWSKY (*Chem. Centr.*, 1901, i, 801; from *Deut. med. Woch.*, 1901, 27, 151).—The author modifies Arnold's method (*Abstr.*, 1900, ii, 113) as follows. After proceeding as far as the addition of 10 or 12 vols. of concentrated hydrochloric acid, he further adds to 15 or 20 c.c. of this mixture 3 c.c. of chloroform and 2—4 drops of ferric chloride solution. As little as 1 part of acetic acid in 40,000 communicates a characteristic violet coloration to the chloroform, which in the absence of acetic acid remains yellowish or feebly reddish. The reaction is not prevented by ordinary therapeutic preparations. M. J. S.

Estimation of Lactic Anhydride in Lactic Acid. By R. KUNZ (*Chem. Centr.*, 1901, i, 791—792; from *Zeit. Oesterr. Apoth. Ver.*, 39, 186).—A 2 per cent. solution of the substance is neutralised with *N*/2 sodium hydroxide, using phenolphthalein as indicator. The alkali consumed corresponds with the lactic acid present and the carboxyl group of the anhydride, $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. An excess of the alkali is then added, and the mixture heated for 5 minutes in the water-bath. This converts the anhydride into sodium lactate. The unconsumed alkali is then titrated by adding an excess of *N*/2 sulphuric acid, warming to expel carbon dioxide, and titrating back. From the first titration there is then subtracted a quantity of alkali equal to that consumed in the second; the remainder gives the lactic acid. Examination of numerous commercial samples shows that they are to a large extent dehydrated, and that the proportion of lactic acid may vary widely without the density being much affected.

M. J. S.

Detection of Salicylic Acid in Wine and Beer. By A. CARDOSO PEREIRA (*Bull. Soc. Chim.*, 1901, [iii], 25, 475—476. Compare this vol., ii, 207).—The author confirms the existence in genuine wines of a substance resembling salicylic acid in its reaction with ferric chloride. The substance is contained in much larger quantity in the marc, from which it is proposed to isolate it. N. L.

Detection of Boiled and Unboiled Milk. By F. UTZ (*Chem. Centr.*, 1901, i, 799—800; from *Pharm. Centr. Halle*, 1901, 42, 149).—The observation of Breteau (*J. Pharm.*, [vi], 7, 569) that the detection of boiled milk by guaiacum tincture is untrustworthy is confirmed. Rubner's method may be used, but Schaffer's (*Schweiz Woch. Pharm.*, 38, 15) is excellent. To 10 c.c. of the milk, 1 drop of a 0.2 per cent. solution of hydrogen peroxide and 2 drops of a 2 per cent. solution of *p*-phenylenediamine solution are added, and the mixture is well shaken.

Unboiled milk immediately becomes blue. Sour milk must first be neutralised with lime water. Buttermilk gives the richest colour, cream gives a greyer blue, whey a violet. Milk which has been heated for a short time at 90° , or a longer time at 70° , does not exhibit the reaction. Traces of formaldehyde delay, larger quantities altogether prevent, the production of the colour; so does an excess of tartaric acid. Ammonium chloride and carbonate have no such effect. M. J. S.

The Guaiacum Test in Practice. By FRIEDRICH GLAGE (*Chem. Centr.*, 1901, i, 861; from *Zeit. Fleisch. und Milchhyg.*, 1901, 11, 162).—According to Ostertag, Arnold's guaiacum test is a trustworthy one for distinguishing between boiled and unboiled milk, and is habitually used in Hamburg during the prevalence of foot and mouth disease. The failure to obtain a blue colour is, however, no proof that the official requirements have been complied with, since these prescribe heating the milk to at least 90° for a quarter of an hour, whilst the test gives a negative result after heating to 80° . The production of a colour is, however, a proof of insufficient heating.

All specimens of tincture of guaiacum do not give the reaction; out of 60 samples tested, less than a third were found suitable. The fitness of the reagent must therefore be ascertained, both at the outset and from time to time. M. J. S.

Calculations Employed in the Analyses of Skimmed and Diluted Milk. By ÉMILE LOUISE and RIQUIER (*Compt. rend.*, 1901, 132, 992—995).—Contains a series of mathematical formulæ applicable to the analysis of sophisticated milk. G. T. M.

Analysis of Sour Milk; Preservation of Milk for the Purpose of Analysis. By A. DUBOIS (*Rev. Intern. Falsif.*, 1901, 14, 42—43; from *Bull. Soc. Pharm. Bordeaux*).—The bottle containing the sour milk which should not have passed beyond the stage of lactic fermentation is heated at 35 — 40° in order to melt the separated fatty matter when it is well shaken. A 200 c.c. flask is taken and milk and water, about 10 c.c. of each alternately, are introduced until the flask contains 100 c.c. of water and 99 c.c. of milk; after thoroughly shaking, a drop of ether is added to destroy the lather, and a few more drops of milk are added to complete the 200 c.c. The author calls this "lait dédoublé." *Specific gravity.* This is taken in a 50 c.c. bottle. From the weight of the milk is deducted 25, and the difference is multiplied by 0.04, which gives the sp. gr. of the original sample. *Acidity.* Twenty c.c. of the mixture are titrated with $N/10$ alkali using phenolphthalein as indicator, and the result calculated to lactic acid. *Lactose.* To 20 c.c. of the mixture are added 3 c.c. of a 5 per cent. solution of sodium metaphosphate and 5 c.c. of hydrochloric acid; after making up to 100 c.c. with water, the filtrate is titrated in the usual way with Fehling's solution. To the percentage of lactose should be added that of any lactic acid in excess of 0.17 per cent. *Casein.* Denigès' process is recommended. *Fat.* Ten c.c. of the mixture are mixed with 1 c.c. of ammonia and 25 c.c. of Adam's ammoniacal ether-alcohol mixture and treated in the same manner as fresh milk. *Total solids.* Twenty c.c. of the mixture are dried in a flat-bottomed

platinum dish on the open water-bath to constant weight. To this is added the weight of the lactic acid; no further corrections need then be applied. *Human milk.* The foregoing applies to human milk except that it is not necessary to dilute in this case. *Preservation of samples.* After several trials, the author now recommends a solution of 50 grams of crystallised phenol in 10 c.c. of alcohol of which 5 c.c. are sufficient to preserve a litre of milk for about 6 weeks. L. DE K.

Composition of Dutch Butter. By JOHN CLARK (*Analyst*, 1901, 36, 113—117).—The paper contains further evidence that the deficiency of Dutch (Friesland) butter in volatile acids, particularly during the months of September, October, and November, is due to natural causes (compare Kirchner and Racine, and Reicher, this vol., ii, 137 and 292). L. DE K.

Halphen's Reaction for Cotton-seed Oil and the Behaviour of some American Lards toward the Same. By PAUL SOLTSIEN (*Zeit. öffentl. Chem.*, 1901, 8, 140—143).—The author has prepared lard from the fatty tissues of two young pigs killed in Chicago, which had been largely fed on cotton-seed meal. These lards gave such a strong reaction with Halphen's sulphur test that they might have been supposed to contain 25 per cent. of cotton-seed oil. They further gave a decided Bechi test and a strong reaction with nitric acid, but gave no reaction with Welmans' phosphomolybdate test. The only proof that they contain no cotton-seed oil was in the fact that they did not yield crystals of phytosterol.

If a lard of unknown origin should give no reaction with Halphen's reagent it may be assumed to be free from, or to contain less than, 0.2 per cent. of cotton-seed oil. But if a reaction is obtained a sample should not be condemned unless there is an indication of the presence of phytosterol. L. DE K.

Heat of Combustion as a Factor in the Analytical Examination of Oils; Heats of Combustion of some Commercial Oils. By H. C. SHERMAN and J. F. SNELL (*J. Amer. Chem. Soc.*, 1901, 23, 164—172).—A table is given showing the heat of combustion per gram (at constant volume and at constant pressure) of 3 samples of raw and 1 of boiled linseed oil, 1 of poppy-seed oil, 3 of maize oil, 6 of cotton-seed oil, 1 of sesamé oil, 3 of rape-seed oil, 2 of castor oil, 1 of peanut oil, 2 of almond oil, 2 of olive oil, 2 of menhaden oil, 2 of cod-liver oil, 1 of whale oil, 4 of lard oil, 1 of sperm oil, 1 of rosin oil, and 3 samples of lubricating petroleum.

The heats of combustion were determined in the Atwater-Blakeslee bomb. The oil was absorbed on a small piece of fibrous asbestos, and ignited directly by the electrically fused iron wire. The whole operation may be finished within an hour. It was found that the heat of combustion is seriously diminished by exposure and oxidation of the samples, which renders it valuable in the technical analysis of oils in conjunction with the other data usually obtained. L. DE K.

A Comparison between the Bromine and Iodine Absorption Figures of Various Oils. By HERMANN T. VULTE and LILY LOGAN (*J. Amer. Chem. Soc.*, 1901, 23, 156—159).—The authors have

redetermined the iodine absorption (Hübl) and the bromine absorption (McIlhiney, *Abstr.*, 1900, ii, 178) of a number of oils and the figures expressed in iodine are given in a table. In some cases there is a fair agreement, but in others the figure calculated from the bromine absorption is greatly in excess of the direct iodine number. The average difference in the case of sweet almond oil was 1.08, of lard oil 1.22, of sperm oil 2.422, of rape oil 4.60, of castor oil 8.01, of seal oil 9.765, of cod-liver oil 10.08, of menhaden oil 10.822, and of rosin oil 48.845.

The average bromine substitution figures of cod-liver oil, menhaden oil, sweet almond oil, sperm oil, castor oil, and rosin oil, were respectively 0.605, 1.245, 2.145, 2.27, 2.63, and 102.345. The high figure for the almond oil may, perhaps, be due to the fact that the sample was somewhat rancid.

L. DE K.

Optical Examination of Fats and Waxes. By GEORG MARPMANN (*Chem. Centr.*, 1901, i, 1015—1017; from *Chem. Rev. Fett. und Harz. Ind.*, 8, 65).—The index of refraction of a mixture is the mean of the indices of its components, regard being paid to their relative proportions. A mixture of equal parts of two substances, a and b , would therefore have an index of refraction $(\mu_a + \mu_b)/2$, and if the index of a is known and that of b unknown, the latter may be calculated from the equation $b = 2(\mu_a + b) - a$. To obtain the refractive indices of substances such as wax, which would, if alone, require to be observed at 70—80°, to the injury of the apparatus, they may be mixed with an oil of known refraction, obtaining a mixture liquid at 40°, and suitable for examination in the butter refractometer. The various fats and essential oils, such as oil of cloves and of peppermint, give good results as solvents, but alcohol and chloroform do not. The purity of a wax cannot with certainty be inferred from its possessing an appropriate index of refraction, since it is easy to make mixtures of the same refractive index, but gross falsifications with paraffin, stearin, tallow, cocoa-fat, or palm oil can be recognised by the refractometer alone. Genuine bees-wax is, however, a very variable substance. A table of refractive indices accompanies the paper.

M. J. S.

Estimation of Fat in Fodders. By M. JAHN (*Zeit. öffentl. Chem.*, 1901, 8, 137—140).—Instead of the ordinary paper cartridge, the author prefers using a case made of tinned iron, 70 mm. high and 19 mm. wide, the bottom of which consists of brass gauze of 35 meshes to the cm. The latter is covered inside with a piece of filter paper and a thin layer of cotton wool, and after 10 or 5 grams of the material to be extracted have been introduced, another layer of cotton wool is placed on the top and then preferably also another disc of wire gauze. The Soxhlet tube most suitable is one 10 cm. high and 2.3 cm. wide and having an overflow of 8.5 cm. The extraction flask should be of the Erlenmeyer type 10 cm. high, 3.5 cm. wide at the top and 7 cm. at the bottom.

The condensed ether drops straight into the case and not being able to escape sideways, must perforce find its way through the mass. When dealing with substances which contain very little moisture and

yield only a small amount of soluble matter to water or alcohol, a previous drying of the material is unnecessary. L. DE K.

Detection of Alkaloids by Microchemical Methods. By E. Pozzi-Escott (*Compt. rend.*, 1901, 132, 920—921).—Contrary to the statements of Popoff (*Rec. trav. Labr. Toxicologie*, 1891), the picrates of the alkaloids, with the partial exception of strychnine picrate, have no characteristic properties that make them available for the detection of alkaloids by the microchemical method.

C. H. B.

Simple Method for the Detection of Caffeine, and its Practical Application. By ANTON NESTLER (*Zeit. Nahr. Genussm.*, 1901, 4, 289—295).—Tea leaves, when carefully heated, yield a sublimate of caffeine, but no sublimate is obtained from exhausted leaves, as the caffeine is very soluble in hot water.

Suspected leaves are reduced to powder, and a little of the powder is heated between two well-fitting watch-glasses, a drop of water being put on the top glass. The watch-glass is put on a wire gauze, and heated by means of the small flame of a Bunsen micro-burner, this being at a distance of 7 cm. from the gauze. After 5 minutes, the inside of the top watch-glass is covered with minute, oily drops, and when the heating is continued for another 5 or 10 minutes, needles of caffeine will make their appearance if the leaves are genuine, but if they have been exhausted no crystals will be visible. The crystals may be further identified, as directed by Molisch, by moistening the sublimate with a drop of hydrochloric acid, and adding a drop of a 3 per cent. solution of gold chloride. The liquid on being allowed to evaporate spontaneously, deposits very characteristic crystals, easily recognised under the microscope; drawings of these are given.

L. DE K.

Proximate Analysis of Cloves. By A. MCGILL (*Analyst*, 1901, 26, 123—126).—Tables are given showing the percentages of *moisture*, *total volatile matter*, *volatile oil*, *total extractive matter*, *fixed oil*, and commercial classification of 8 samples of Penang and 18 of Amboyna cloves.

The moisture was estimated by exposing 2 grams of the powdered sample for 24 hours over sulphuric acid under a pressure of 60 mm. of mercury. Total volatile matter was determined by heating 2 grams of the sample at 98° for 24 hours in a current of dry air. It was found that the loss is much increased when the sample is first moistened with 25 c.c. of ether, which is then allowed to evaporate spontaneously; after drying at 98°, the mass should be again treated with ether. The total extractive matter was obtained by extraction in a Soxhlet apparatus to constant weight. A check on the volatile oil was attempted, by evaporating the solvent and drying the extract, first at a low temperature, and then at 100°, but it was found to be impracticable.

The volatile oil, which is the most essential constituent, and which should not fall below 14 per cent., was obtained from the difference between the volatile matter and the moisture.

L. DE K.

General and Physical Chemistry.

Sensitiveness to Light of Fluorescein, its Substituted Derivatives and the Leuco-bases. By OSCAR GROS (*Zeit. physikal. Chem.*, 1901, 37, 157—192).—The leuco-bases of a number of coloured derivatives of triphenylmethane were found to be sensitive to light, and by the use of coloured glasses it was found that darkening proceeded most rapidly under rose-coloured glass. Addition of salts generally causes an increase of sensitiveness. The bleaching of the dyes themselves was also investigated and found to be associated with absorption of oxygen, and hence most probably to be due to oxidation processes. The effects of substituents on the sensitiveness of the leuco-base of fluorescein were investigated; the nitro-group causes a great increase of sensitiveness, the nitro-compounds examined rapidly oxidising in the dark, whereas with the other compounds little or no action takes place in the absence of light. The presence of the dye itself, if not in too great a quantity, was found to cause in general an increase in the oxidation velocity of the leuco-base. Foreign dyes were also found to accelerate the oxidation of both dye and leuco-base, this action being evident at very high dilutions. It was further found that dyes accelerate also other reactions which are sensitive to light, for example, the reduction of mercuric chloride by ammonium oxalate. Metallic salts have but a slight catalytic action, copper salts being remarkable in causing an increase of sensitiveness in ammoniacal solution and a decrease in acid solutions.

L. M. J.

Band Spectrum of Nitrogen in Oscillatory Spark. By G. A. HEMSALECH (*Compt. rend.*, 1901, 132, 1040—1043).—When a high self-induction is inserted in the circuit, the spectrum obtained by means of a condenser discharge between various metals yields a number of bands which the author had previously considered to be due to nitrogen; the careful measurement of the wave-lengths has now proved this view to be correct, the bands being identical with those obtained at the negative pole of a Geissler nitrogen tube.

L. M. J.

Jahn's Measurement of the *E.M.F.* of Concentration Cells. By R. A. LEHFELDT (*Zeit. physikal. Chem.*, 1901, 37, 308—314).—The *E.M.F.* of a concentration cell may be expressed as a function of the total concentration of the electrolyte at the cathode and anode, the degree of dissociation, and the mobility of the ions (this vol., ii, 4): (1) $E = f_1(C, \gamma, x)$. Nernst's formula (2), $E = f_2(\gamma C, x)$, apparently contradicts this. If we express Ostwald's dilution law by (3), $\gamma = f_3(C)$, then from (1) and (3) we get (2) which shows that Nernst's formula does not contradict but is contained in (1). Jahn by assuming $\gamma = 1$ for dilute solutions is able to calculate the value of γC for other solutions. As, however, (3) is contained in (2), this is necessarily the case, and the agreement between Jahn's values for the dissociation constants signifies nothing. The author regards it as correct only to apply

equation (1), and if the results calculated for γ do not agree with those of (3) then (3) and consequently also (2) do not apply to the electrolyte under consideration. Jahn's results have been recalculated, but it is not possible to draw definite conclusions as to whether Ostwald's dilution law applies rigorously to strong electrolytes. J. McC.

Electric Battery with a Depolariser which is spontaneously regenerated by Direct Reoxidation by the Air. By GEORGES ROSSET (*Bull. Soc. Chim.*, 1901, [iii], 25, 541—543).—The negative pole of the cell consists of a zinc rod immersed in ammonium chloride solution, whilst the positive copper pole is placed in a porous cell containing an ammoniacal solution of copper oxide. The hydrogen liberated at the cathode reduces the cupric to the cuprous compound which, having a lower density, rises to the surface of the liquid and is re-oxidised by the oxygen of the air. The loss of ammonia which occurs in these reactions is replaced by that set free by the action of the ammonium chloride on the zinc. N. L.

Conductivity produced in Hydrogen and Carbon Dioxide by the Motion of Negatively charged Ions. By JOHN S. TOWNSEND and P. J. KIRKBY (*Phil. Mag.*, 1901, [vi], 1, 630—642).—In continuation of previous work (Townsend, this vol., ii, 221), the authors find that the phenomena which characterise the conductivity of air at low pressures are met with also in the case of hydrogen and carbon dioxide. From the results obtained, it is found that the mean free path of an ion is longer than that of a molecule in the following ratios, 4·8 : 1 for hydrogen, 4·6 : 1 for carbon dioxide, 4·3 : 1 for air. It appears that approximately the same energy is necessary to ionise a mol. of carbon dioxide and a mol. of air, whilst less energy is required to ionise hydrogen. J. C. P.

Change of Conductivity with Temperature up to and above the Critical Temperature in Solutions of Salts in Liquid Sulphur Dioxide. Electrolytic Conduction in Gases and Vapours. Absorption Spectra of Solutions of Iodides. By AUGUST HAGENBACH (*Ann. Phys.*, 1901, [iv], 5, 276—312).—Solutions of salts in liquid sulphur dioxide are electrolytes (compare Walden, *Abstr.*, 1900, ii, 10), and retain this property up to and over the critical temperature; that the compressed gas solution thus obtained contains ions is shown by the polarisation. Superheated and saturated vapours above a solution behave in a similar manner. The temperature co-efficients for sodium and potassium iodides, potassium bromide and chloride, are regularly negative for the interval 20—160° except in the case of potassium iodide, which exhibits a maximum of conductivity about 90°. The temperature coefficients become numerically very large towards the critical temperature, but become smaller again above that point. The conductivity of the saturated vapour shows a maximum at the critical temperature. When a closed vessel fitted with electrodes and containing a salt solution in sulphur dioxide is shaken, the needle of the galvanometer swings from side to side if the temperature is below the critical point, but remains steady if the temperature is above

the critical point; the critical temperature of these solutions is thus capable of very exact determination.

Solutions of iodides in liquid sulphur dioxide are generally red, but sometimes yellowish in colour. From the spectroscopic investigation, the author concludes that the salts in solution have an absorption spectrum belonging either to the ions or to the undissociated molecules.

A few experiments with aqueous solutions showed that it is impossible to obtain exact results on the same lines as those indicated above.

J. C. P.

Ionisation of Atmospheric Air. By C. T. R. WILSON (*Proc. Roy. Soc.*, 1901, **68**, 151—161).—There is a continual leakage of electricity from a charged conductor suspended in a vessel containing dust-free air. The rate of leak is (1) approximately proportional to the pressure, (2) the same in the dark as in diffuse light, (3) the same for positive and negative charges. The loss of charge per second is the same whether the initial potential is 120 or 210 volts, and is such as would result from the production of about 20 ions of either sign in each cubic centimetre per second in air at atmospheric pressure (compare Geitel, *Physikal. Zeit.*, 1900, **2**, 116—119).

J. C. P.

Electro-capillary properties of some Organic Compounds in Aqueous Solution. By A. GOUY (*Compt. rend.*, 1901, 132, 822—824).—If H be the maximum height of the column in the capillary-electrometer and H' the height after the addition of the compound, the value $d = 1000(H - H')/H$ is taken as measure of the lowering of the electro-capillary maximum, and the values were found for a large number of organic compounds at dilutions varying from $M/1$ to $M/1000$. The solutions were not made with pure water but with a decinormal solution of sodium sulphate, although it was found that similar values are obtained with solutions, if sufficiently dilute, of any other electrolyte. It was found that this constant varies very greatly for different compounds, even isomerides, whilst great differences are also obtained for the effect of dilution as, for example, propyl alcohol; $M/1$, 59; $M/10$, 7:—dextrose; $M/1$, 40; $M/10$, 24. The author hence considers that a further study of this constant should prove interesting and useful. The phenomenon of electro-capillary viscosity was also observed for these organic compounds (see this vol., ii, 83).

L. M. J.

Calculation of Degree of Dissociation of strong Electrolytes. II. By SVANTE ARRHENIUS (*Zeit. physikal. Chem.*, 1901, **37**, 315—322. Compare this vol., ii, 144).—In defending the views previously expressed, the author points out that many of the criticisms of Jahn (*Zeit. physikal. Chem.*, 1901, **36**, 453) and Nernst (*Zeit. physikal. Chem.*, 1901, **36**, 596) are based on misunderstandings of the author's statements.

Making use of the experiments of Loomis (*Abstr.*, 1894, ii, 228) and Hausrath (*Inaug. Dissert. Göttingen*, 1901) with solutions of hydrochloric acid, potassium chloride, and sodium chloride, it is shown that these are in agreement with the author's formula for the calculation of the *E.M.F.* of concentration cells if in this van't Hoff's ionisation

constant i be replaced by the value $1 + a$ found from the conductivity ($\alpha = \mu_v / \mu_\infty$). In the cases referred to, it is therefore justifiable to set $i = 1 + a$; but the author believes that this is not quite general, since cases are known in which i does not diminish with increasing concentration so rapidly as does $1 + a$. J. McC.

Progressive Change of the Factor i as a Function of the Concentration. By A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 717—722. Compare this vol., ii, 304).—Of the salts previously investigated by the author, potassium nitrate was the only one for which the factor i decreased with increasing concentration. With the boiling point method, it has now been found that the nitrates of sodium, barium, silver, and lead behave like potassium nitrate, whilst in the case of strontium nitrate, i tends to increase with the concentration. J. C. P.

Vapour Pressure of Ternary Systems. By FRANZ A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1901, 37, 129—156).—A continuation of previous papers (this vol., ii, 146, 224, 305, 372). In the present paper, the system Liq. + Liq.₂ + Vapour is considered, and the effect of distillation either at constant temperature or at constant pressure. It is shown that, if a pressure maximum exists, the composition of both liquid layers will change during distillation in such a manner as to approximate to those corresponding with the maximum pressure. If a minimum pressure exists, the composition during distillation approaches that of either of the critical liquids, whereas if neither maximum nor minimum exists, the composition approximates to that of the critical liquid which possesses the lower vapour pressure. L. M. J.

Vapour Pressure of Mixed Crystals of Isomorphous Salts. By REINHARD HOLLMANN (*Zeit. physikal. Chem.*, 1901, 37, 193—213).—It has been previously shown that in some cases the vapour pressure of a hydrated salt is lowered by the union with it of an isomorphous salt to form mixed crystals, and this phenomenon is more fully investigated. The vapour pressures of the salts were obtained by determining the composition of the sulphuric acid solution possessing equal vapour pressure (Müller-Erbach, *Abstr.*, 1896, ii, 295), and curves are given for vapour pressure against composition of the mixed crystals. The first case examined was that of mixtures of potassium aluminium alum and iron alum; the vapour pressures of the pure salts are respectively 2 mm. and 10.9 mm., whilst for the mixtures, two minima occur at 1.4 mm. and 7.9 mm., and a maximum of 8.1 mm., the latter occurring with crystals of the composition Fe:Al = 2:1. Similar results are obtained when chrome alum replaces the iron alum. With mixtures of magnesium and zinc sulphates, two maxima occur for Mg:Zn = 2:1 and Mg:Zn = 1:1 respectively. In the case of mixtures of copper and manganese sulphates, the results are more complicated owing to the existence of two sets of mixed crystals, and only portions of the curves are obtainable with intervening gaps, whilst similar results are obtained for mixtures of sulphates of zinc and copper, magnesium and copper, zinc and manganese. In all cases,

however, the existence of maxima are indicated. The author considers these maxima correspond with definite double salts, and may be taken as a proof of their existence. The results indicate further that as a general rule the vapour pressure of a hydrated salt is lowered by union with an isomorphous salt.

L. M. J.

Cryoscopic Investigations with Inorganic Solvents. By STANISLAW TOLLOCZKO (*Bull. Acad. Sci. Cracow*, 1901, 1—22. Compare Abstr., 1900, ii, 190).—In order to test Brühl's hypothesis (Abstr., 1899, ii, 10), the author has investigated the dissociating power of antimony trichloride, antimony tribromide, arsenic tribromide, and stannic bromide by the cryoscopic method. A similar investigation has been carried out by Walden (this vol., ii, 11), and by both the hypothesis of a connection between unsaturated character and dissociating power is unsupported. Of the solvents examined, only antimony chloride has a strong dissociating influence on inorganic salts. Arsenic bromide possesses the power also, but in a markedly less degree. The author regards it as possible that the abnormal depression noticed with these solvents may be due to chemical action, and suggests that arsenic triiodide in antimony chloride may give rise to an increased number of active molecules by the following reaction: $\text{AsI}_3 + 3\text{SbCl}_3 = \text{AsCl}_3 + 3\text{SbCl}_2\text{I}$; thus the number of molecules different from the solvent is increased fourfold, and this agrees with the molecular weight (625) calculated from the observed depression of the freezing point.

By addition of bismuth bromide to antimony bromide, of bismuth chloride to antimony chloride, and of antimony bromide to arsenic bromide, the freezing point is raised (similarly to β -naphthol in naphthalene).

At low concentrations, sulphur exists as S_8 and iodine as I_2 in antimony chloride.

The latent heats of fusion have been determined for antimony chloride (13.37 cal.) and for antimony bromide (9.73 cal.). The values for the molecular depression calculated by van't Hoff's formula with these numbers agree well with those found experimentally.

J. McC.

Polymerisation of Organic Liquids. By PHILIPPE A. GUYE and ACHILLE BAUD (*Arch. Sci. Phys. Nat. Geneve*, 1901, [iv], 11, 449—471).—As the experiments of Dutoit and Frederich (Abstr., 1900, ii, 194) have shown that the temperature coefficient of the surface tension is not the same for different liquids, the authors have added further data. The method of determination was similar in nature to that adopted by Ramsay and Shields, the calibration of the capillary being effected by measurement of the elevation of benzene in different parts of the tubes. The following are the results obtained for the density: molecular surface energy, γ ; temperature coefficient of molecular surface energy, k ; and complexity coefficient, x (see Ramsay and Shields, *Trans.*, 1893, 1089). Anisole, $d_t = 0.9951 - 0.0,896(t - 16.7^\circ) - 0.0,56(t - 16.7^\circ)^2$; $\gamma(9^\circ) = 803.45$, $(152.9^\circ) = 482.59$; $k = 2.358, 2.315, 2.229$; $x = 0.85, 0.87, 0.92$. Phenetole, $d_t = 0.9659 - 0.0,396(t - 20.8^\circ) - 0.0,33(t - 20.8^\circ)^2$; $\gamma(19.2^\circ) = 819.9$, $(152.4^\circ) = 504.22$; $k = 2.563, 2.376, 2.370$; $x = 0.75, 0.84, 0.94$. Methylurethane, $d_t = 1.1361 - 0.00107$

($t - 55.4^\circ$); $y(55.9^\circ) = 612.47$, (150.9°) = 464.55; $k = 1.564, 1.557$; $x = 1.57, 1.58$. Ethylurethane, $d_{75^\circ} = 1.0336$, $d_{105^\circ} = 1.0031$, $d_{145^\circ} = 0.9600$; $y(65.1^\circ) = 587.81$, (152.6°) = 453.3; $k = 1.500, 1.537$; $x = 1.68, 1.62$. *iso*Propylurethane, $d_{65^\circ} = 0.9961$, $d_{105^\circ} = 0.9575$, $d_{155^\circ} = 0.9068$; $y(65.5^\circ) = 610.0$, (152.4°) = 481.16; $k = 1.488, 1.494$; $x = 1.701, 1.691$. Phenylurethane, $d_{65^\circ} = 1.0770$, $d_{105^\circ} = 1.0423$, $d_{155^\circ} = 0.9968$; $y(63.8^\circ) = 857.09$, (152.8°) = 695.9; $k = 1.382, 1.810$; $x = 1.90, 1.26$. Methyl ethyl ketoxime, $d_t = 0.9385 - 0.0_88814t - 0.0_6428t^2$; $y(13.8^\circ) = 605.4$, (150.4°) = 366.8; $k = 1.746$; $x = 1.33$. Valeroxime, $d_t = 0.8962 - 0.0_889(t - 15.6^\circ) - 0.0_618(t - 15.6^\circ)^2$; $y(16.2^\circ) = 636.66$, (152.2°) = 401.7; $k = 1.825, 1.709, 1.727$; $x = 1.25, 1.39, 1.35$. Nitrobenzene, $d_t = 1.2075 - 0.0_8845(t - 11^\circ) - 0.0_5125(t - 11^\circ)^2$; $y(9.4^\circ) = 954.5$, (153°) = 650.8; $k = 2.124, 2.165, 2.114$; $x = 0.99, 0.96, 1.01$. Benzonitrile, $y(8^\circ) = 861.4$, (152.4°) = 561; $k = 2.226, 2.068, 2.080$; $x = 0.93, 1.04, 1.02$. *m*-Cresol, $y(9^\circ) = 840.6$, (153.1°) = 575.1; $k = 2.053, 1.811, 1.842$; $x = 1.05, 1.26, 1.23$. Ethyl acetate, $y(9.5^\circ) = 519.16$, (77°) = 373.0; $k = 2.302, 2.165$; $x = 0.88, 0.96$. Only the lowest and highest values of y are here given, and the first values of k and x refer to the lower temperature intervals.

L. M. J.

The Critical State. By INNOCENTIUS I. KANONNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 197—229).—The author discusses the critical state in relation to van der Waals' equation and from the critical data of a large number of compounds as given by various authors, and from a consideration of their true density (see Abstr., 1900, ii, 134, and this vol., ii, 305) in the critical condition, he arrives at the following conclusions: (1) The critical volume is double the constant b of van der Waals' equation. (2) This constant b depends directly on the true volume occupied by a molecule of the compound, the relation being expressed by the equation: $b = 4\sqrt{2} \cdot r \cdot d$, where r is Lorenz and Lorentz's constant; $(\mu^2 - 1)/(\mu^2 + 2)d$, and d the theoretical density of the substance. (3) In the critical state, the valencies of carbon and oxygen undergo change, the former element becoming sexa-valent, and the latter quadri- and even sexa-valent. (4) Under critical conditions, compounds have the same structure and are in the same state as they are in dilute solutions. A table is given showing for a series of 52 compounds the values of the various critical constants and of the constants a and b of van der Waals' equation.

T. H. P.

Isochores of Ether from 1 c.c. to 1.85 c.c. By EDOUARD MACK (*Compt. rend.*, 1901, 132, 1035—1037).—The relationship between volume, pressure, and temperature has been completely determined between the limits $v = 1$ c.c. to 1.85 c.c. and $t = 100^\circ$ to 206° . The expression $p = at + \beta$ at constant volume was found to be valid, the divergences being within the experimental errors. Where comparable, the results are found to agree well with those of Ramsay and Young.

L. M. J.

Relation between Viscosity and some other Physical Constants. By A. BATSCINSKI (*Zeit. physikal. Chem.*, 1901, 37, 214—216).—The author deduces that for all compounds $M^{1/2} \theta^{1/2} / \eta T$ (MR),

= constant, where M is the molecular weight, θ the critical temperature, η the viscosity coefficient, and R the specific rotation. The values of the constants are calculated for fifteen organic compounds, comprising hydrocarbons, chlorides, aldehydes, ethers, and esters; they only vary between the limits 37.4 and 41.3. From the mean value 39.5, the author recalculates the critical temperatures, and the values show a close approximation to the experimental numbers.

L. M. J.

Relation between Osmotic Pressure and Osmotic Work. By KONRAD DIETERICI (*Zeit. physikal. Chem.*, 1901, 37, 220—222).—A reply to Noyes (this vol., ii, 87).

L. M. J.

Osmosis across a Membrane of Copper Ferrocyanide. By G. FLUSIN (*Compt. rend.*, 1901, 132, 1110—1112).—The velocity of osmosis was determined for solutions of dextrose, sucrose, amygdalin, antipyrine, and carbamide. This naturally varies with the form and dimensions of the vessel, but when the same vessel is used for different solutions it is shown that the ratio of the osmotic velocities is equal to the ratio of the osmotic pressures of the solutions. No results are obtainable with carbamide inasmuch as it is proved that the copper ferrocyanide membrane is permeable to it.

L. M. J.

Solubility of Gases in Organic Solvents. By GERHARD JUST (*Zeit. physikal. Chem.*, 1901, 37, 342—367).—The object was to ascertain whether there is any relationship between the absorption coefficients of different gases in the same liquids, for instance, whether the order of solubility of various gases is the same in various liquids.

The solubility of carbon dioxide in 44 solvents at 15°, 20°, and 25° has been determined. The lowest solvent power is shown by glycerol, then follows water, whilst methyl acetate dissolves about eight times as much of the gas as water does. The solubility in any homologous series of solvents diminishes with increase of molecular weight of the solvent. In a mixture of equal volumes of benzene and alcohol, or of benzene and chloroform, the solubility is the arithmetic mean of the solubility in the separate constituents. This does not, however, hold for all mixtures.

The solubility of hydrogen, nitrogen, and carbon monoxide has been determined in 17 solvents. The results indicate that if the solvents are arranged in the order of their solvent power for each of the four gases, practically the same series is obtained in each case.

Between 15° and 25°, the solubility of hydrogen, nitrogen, and carbon monoxide increases with rise of temperature; in the case of carbon dioxide, the solubility diminishes as the temperature rises through the same interval.

Connections are drawn between solvent power and other physical constants of liquids.

J. McC.

Theory of Colloidal Solution. By FREDERICK G. DONNAN (*Phil. Mag.*, 1901, [vi], 1, 647—652).—In attempting to explain the different behaviour of crystalline and colloidal substances towards liquid media, the author emphasises the distinction between kinetic-molecular equilibrium and statical equilibrium at the interface of solid and liquid.

Thus, when a crystalline solid is dissolving in a liquid medium, the resultant mechanical force acting inwards on a small volume-element at the interface of solid and liquid, preserves the molar integrity of the mass, even though molecular disintegration is taking place. In the solution of colloidal substances, the author sees a case where, up to a certain point, the forces tending to molecular disintegration are greater than those which tend to preserve the molar integrity; in other words, the molecular adhesion between the liquid medium and the colloid is greater than the molecular cohesion of the colloid itself. It is further assumed that the intermolecular attractive forces fall off more rapidly with increasing distance in the case of the molecular cohesion of the colloid than in the case of the adhesion of the colloid and the surrounding medium. There will therefore be a certain critical dimension at which the disintegration of the colloid will cease (before it reaches the molecular limit), and a two-phase system results consisting of the colloid distributed through the original liquid medium in a state of very fine division. For dimensions of the colloid larger than the critical, its common surface with the surrounding medium will tend to increase, whilst for dimensions less than the critical there will be a positive surface tension. J. C. P.

Salt Precipitation by Vaporisation of Dilute Solutions. By FREDERICK W. SKIRROW and HARRY T. CALVERT (*Zeit. physikal. Chem.*, 1901, 37, 217—219).—The various cases which may occur during the boiling of a salt solution are considered with the aid of curves representing boiling point against concentration and solubility, that is, concentration against temperature. If these curves intersect, salt precipitation occurs when the conditions represented by the point of intersection are attained. If, however, the curves do not cut, no precipitation occurs, the temperature rising continuously until the melting point of the salt is reached; precipitation may, however, occur by diminution of pressure. The solubility curve may further cut the boiling point curve in two points, in which case precipitation of the salt takes place at the lower point and solution at the higher. L. M. J.

Velocity of Chemical Reactions. By WILLIAM DUANE (*Amer. J. Sci.*, 1901, [iv], 11, 349—356).—The author describes two new methods of measuring the rate of inversion of sugar. The basis of the first method is the change in the index of refraction accompanying inversion. A tube with plane glass ends (not quite parallel) is divided into two wedge-shaped compartments, one of which is filled with the solution to be inverted, the other with an already inverted solution. Light from an illuminated slit passes through a long focus lens and through the tube just described, and forms a distant image. The movement of this image as the solution is inverted is recorded photographically, and from the curve obtained the velocity constant may be calculated. The results obtained by the author give values for the velocity constant which decrease as the inversion proceeds.

The second method depends on the change of volume accompanying inversion. The solution to be examined fills a spiral tube closed at one end, and connected at the other with a horizontal capillary tube containing a column of mercury to indicate the change of volume.

On the assumption that the change of volume is proportional to the amount of sugar inverted, the velocity constant may be calculated. The values obtained by the author show a tendency to decrease as the inversion proceeds.

J. C. P.

Inversion of Cane Sugar. By HANS EULER (*Ber.*, 1901, 34, 1568—1572).—A reply to von Lippmann (this vol., ii, 89).

J. J. S.

Dynamic Investigation of the Bromination of Aromatic Compounds. By LUDWIK BRUNER (*Bull. Acad. Sci. Cracow*, 1901, 22—59. Compare *Abstr.*, 1900, ii, 647).—The reaction between bromine and benzene is unimolecular and is not affected by excess of benzene. The influence of several bromine carriers has been investigated; many of these act catalytically, chromic chloride and metallic chromium being exceptions. Aluminium salts have the greatest catalysing effect, then follow thallium salts, iron salts, iodine, antimony, and phosphorus haloids. Water also acts as a catalyser, and consequently in bromination its presence is advisable. The series given applies also to the influence of the catalysers on the reaction between bromine and monobromobenzene, but not with nitrobenzene, aniline, or phenol; this shows that the effect of the catalyser is dependent on the nature of the substance to be brominated.

The author discusses the theory of catalysis and brings forward experimental evidence of the formation of an intermediary product in the case of the catalysis by iodine. Iodine monobromide gives more bromobenzene than a mixture of equivalent quantities of bromine and iodine in the same time.

The relative speeds of the quick reactions between phenol, *p*-bromophenol, or aniline and potassium iodide and bromine in aqueous solution have been determined. The author finds that $k_1/k_2 = \{x_1(b-a)/(a-x_1)\} \cdot 1/[\ln.a(b-x_2)/b(a-x_2)]$ is constant, where a is the concentration of potassium iodide and of bromine (equivalent), b is the concentration of phenol (or aniline), x_1 is the amount of iodine separated, and $x_2 (= a - x_1)$ the amount of phenol brominated. For phenol, $k_1/k_2 = 5$, which indicates that the separation of iodine from potassium iodide by bromine takes place five times as quickly as the bromination of phenol. For aniline, $k_1/k_2 =$ about 2, showing that aniline is more easily brominated than phenol. The author compares the speed of bromination of phenol and of aniline with the velocity of reactions between ions.

J. McC.

Inorganic Ferments. II. Catalytic action of Platinum as affected by Poisons. By GEORG BREIDIG and KIKUNAYE IKEDA (*Zeit. physikal. Chem.*, 1901, 37, 1—68. Compare Bredig and Müller von Berneck, *Abstr.*, 1900, ii, 213).—The analogy between the catalytic action of colloidal platinum and that of organic ferments (*loc. cit.*) is followed out, especially in connection with the effect of poisons. The rate of decomposition of hydrogen peroxide in presence of colloidal platinum is extraordinarily influenced by substances like hydrocyanic acid, hydrogen sulphide, and mercuric chloride, even in minute quantities; thus the catalytic effect of a platinum solution is halved by

hydrocyanic acid, even when the concentration of the latter is only 0.0014 milligram per litre. The following substances act as strong "poisons" towards colloidal platinum; hydrocyanic acid, iodine cyanide, iodine, mercuric chloride, hydrogen sulphide, sodium thiosulphate, carbon monoxide, phosphorus, hydrogen phosphide, arsenic hydride, mercuric cyanide, and carbon disulphide; the effect of hydrocyanic acid, carbon monoxide, phosphorus, and hydrogen phosphide is temporary, and the platinum gradually recovers. The following are moderately strong "poisons": aniline, hydroxylamine, bromine, hydrogen chloride, oxalic acid, amyl nitrite, arsenious acid, sodium sulphite, and ammonium chloride. The following are weak "poisons": phosphorous acid, sodium nitrite, nitrous acid, pyrogallol, nitrobenzene, hydrogen fluoride, and ammonium fluoride. Formic acid, hydrazine, and dilute nitric acid intensify the catalytic action of colloidal platinum, whilst dilute potassium chlorate solution, ethyl alcohol, amyl alcohol, ether, glycerol, turpentine, and chloroform have practically no effect.

Blood may act as the catalytic agent in the decomposition of hydrogen peroxide, and from results obtained by Schaer it is seen that the parallelism between the poisoning of blood and of colloidal platinum is quite marked.

The "poisoning" of colloidal platinum by the above-mentioned substances may be due to one of four causes. (1) If it be assumed that for the catalytic decomposition of hydrogen peroxide the presence of oxygen in the platinum is necessary, either dissolved or chemically united (compare Haber and Grinberg, *Abstr.*, 1899, ii, 17), then the effect of reducing substances like hydrogen sulphide, hydroxylamine, and phosphorus is easily understood. (2) The surface of the platinum may be chemically or mechanically changed by the deposition of some layer, such as sulphur from hydrogen sulphide, and calomel or mercury from mercuric chloride. (3) The platinum may be chemically attacked and dissolved, for example, by hydrocyanic and hydrochloric acids. The quantity of platinum present, however, is often far in excess of the "poisonous" substance. (4) The surface of the platinum may be so affected that the potential difference between it and the solution, and consequently its surface tension, may be altered. This might be due to the formation of complex substances (such as H_2PtCy_4), or to the removal of oxygen from the surface of the platinum by carbon monoxide, amyl nitrite, and others of the "poisons." J. C. P.

Inorganic Ferments. III. Catalysis of Hydrogen Peroxide by Gold. By GEORG BREDIG and W. REINDERS (*Zeit. physikal. Chem.*, 1901, 37, 323—341. Compare *Abstr.*, 1900, ii, 213).—A colloidal solution of gold is obtained when a current is passed between gold wires in a dilute solution (0.001 *N*) of sodium hydroxide. The solution has a bluish-violet colour, and contains 1 gram atom of gold in 1360 litres.

The influence of this solution on the catalysis of hydrogen peroxide at 25° has been determined, and the results are, on the whole, similar to those obtained with colloidal platinum solution. In neutral solution, the catalytic effect is very small, but in alkaline solution the decomposition is greatly accelerated. The effect is proportional to the

concentration of the alkali up to a maximum (about $1/64 N$ NaOH), and further increase of alkali diminishes the speed. The influence of gold on the reaction in alkaline solution can still be detected when the concentration of the gold is only 0.0003 mg. per c.c. The acceleration is not proportional to the concentration of the gold.

Electrolytes in general diminish the catalytic action of colloidal gold. Hydrogen sulphide, potassium cyanide, sodium sulphite, and sodium thiosulphate "poison" the solution, but in presence of hydrogen peroxide the gold recovers its catalysing influence. Mercuric chloride, which is one of the strongest poisons for colloidal platinum, exerts the opposite effect on the catalysing power of colloidal gold in alkaline solution. Mercuric chloride alone has no catalysing action, but in presence of colloidal gold in alkaline solution the hydrogen peroxide reduces the mercuric salt to mercury (colloidal), and the acceleration produced by gold and mercuric chloride may be due to the catalysis by mercury, which is probably very great. J. McC.

Catalysis in the Reaction between Hydrogen Peroxide and Hydriodic Acid. By JOHANNES BRODE (*Zeit. physikal. Chem.*, 1901, 37, 257—307).—The influence of various agents on the rate of separation of iodine from hydriodic acid by hydrogen peroxide has been determined. From the results of Noyes and Scott (*Abstr.*, 1896, ii, 158), it is clear that the velocity is directly proportional to the concentration of the hydrogen peroxide and of the iodine ions. Since in the reaction hydrogen ions disappear, it was to be expected that the velocity would be proportional to the concentration of these, and Noyes has formulated the catalytic influence $dx/dt = (k + k'c_H)c_{H_2O_2}c_I$. Experiments with various acids have proved that the ratio between the hydrogen ion concentration and the acceleration is constant, in conformity with Noyes' view that the hydrogen ions only exert a catalytic influence which is proportional to the concentration.

Ferrous sulphate greatly increases the velocity of the reaction, and the increase is almost proportional to the concentration. Ferrous sulphate with sulphuric acid, or with sulphuric acid and sodium sulphate, increases the velocity to a slightly greater extent at low concentrations than ferrous sulphate alone, but as the concentration increases the catalytic influence of the pure salt increases more rapidly than when the mixed catalyser is used. This is probably due to the retrogression of the dissociation of ferrous sulphate on account of the increase of the concentration of the SO_4 ions. Schönbein's observation that ferrous sulphate in neutral solution is a better catalyser than in acid solution has been confirmed.

In acetic or oxalic acid solution, the action of iron ions is greatly reduced. Copper sulphate exerts scarcely any effect on the catalysis, but addition of this salt, even in minute quantity, to ferrous sulphate vastly increases the influence of the latter on the reaction.

Molybdic and tungstic acids enormously increase the velocity of the reaction, thus molybdic acid at a concentration of 1 gram-mol. in 1,000,000 litres more than doubles the speed. The accelerations which these two acids produce in equivalent concentrations are about the same in strongly acid solution. They differ, however, inasmuch

as tungstic acid exhibits the phenomenon of hysteresis. It is probable that the influence of these acids is connected with their power of forming peracids, but it is remarkable that other peracid-forming substances such as sulphuric acid, and boric acid, have no catalytic action.

Ferrous sulphate and molybdic acid, and molybdic and tungstic acids, when mixed, produce an additive influence, but ferrous sulphate exerts a retarding effect on the action of tungstic acid.

In the case of hydrogen ions we have a purely catalytic action, but with other catalysers ("pseudocatalysers") it is not improbable that intermediate reactions take place. Assuming, in the case of molybdic acid, that the velocity of the first reaction is very great compared with that of the second, then the acceleration will be measured by the velocity of the second reaction, which is between permolybdic acid and hydriodic acid. If the latter reaction be of the second order, then its velocity is expressed by $dx_1/dt = k'c_{\text{catalyser}}c_I$. According to the principle of co-existence, we must add to this the velocity of the pure reaction (between H_2O_2 and HI), $dx/dt = kc_{\text{H}_2\text{O}_2}c_I$, and so obtain $(dx + dx_1)/dt = k(c_{\text{H}_2\text{O}_2} + k'/k \cdot c_{\text{catalyser}})c_I$. Or, setting $(dx + dx_1) = dx_2$ and $k'/k = \gamma$, $dx_2/dt = k(c_{\text{H}_2\text{O}_2} + \gamma c_{\text{catalyser}})c_I$. The author finds from experiments with molybdic acid that γ has a constant value, and concludes that the premises are correct, namely, that in the first place hydrogen peroxide oxidises the molybdic acid. The formula apparently does not hold for the catalysis with a mixture of ferrous sulphate and molybdic acid, and this is attributed to the disturbance caused by the free iodine on the equilibrium: $\text{Fe}''' + \text{I} \rightleftharpoons \text{Fe}'' + \text{I}$.

Incidentally, the author has investigated the distribution of hydrogen peroxide between ether and molybdic acid solutions, and the results show that permolybdic acid is formed in solution, and even at high dilution is not hydrolysed to molybdic acid and hydrogen peroxide. Distribution experiments with iron salt solutions and with tungstic acid solutions have not led to definite results. J. McC.

Catalysis in Concentrated Solutions. By JAMES M. CRAFTS (*Ber.*, 1901, 34, 1350—1361; *J. Amer. Chem. Soc.*, 1901, 23, 236—249).—The author has studied the rate of hydrolysis of certain sulphonic acids (chiefly *m*-xylenesulphonic acid) in solutions containing from 10 to 38 per cent. of hydrogen chloride. The acids were heated in a sealed tube at 100°, and the amount of hydrocarbon separated was noted from time to time. The rule that holds for dilute solutions, namely, that the velocity of the reaction is proportional to the concentration of the catalytic agent, is quite inapplicable in the cases examined by the author; for *m*-xylenesulphonic acid he finds that when the concentration of hydrogen chloride is within the limits 13 and 31 per cent., an increase of 6 per cent. in that concentration leads to a velocity constant four times its previous value. Experiments to be described later extend the application of this rule to other sulphonic acids, and to solutions with less than 13 per cent. of hydrogen chloride. Another remarkable fact is that when a 38 per cent. solution of hydrogen chloride has added to it the half of its weight of zinc chloride, the velocity of reaction is quadrupled. The author doubts whether the term 'catalysis' correctly describes these phenomena, and

hopes to give a new theory of the reaction when the experimental data are more numerous. The study of the behaviour of various sulphonic acids under the above conditions is important, since it may lead to new methods of separating the corresponding hydrocarbons.

J. C. P.

Equilibria in Ternary Systems. By FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 701—714).—A discussion of some points raised by the author's previous investigation of the system, water-phenol-acetone (*Abstr.*, 1900, ii, 393). In particular, it is shown how the position of the chords of the connodal curve at 56.5° may be determined. Attention is drawn to the fact that, whilst the vapour pressure of water is raised, that of a water-acetone mixture is lowered by the addition of small quantities of phenol. Theoretical considerations show that the addition of a new substance to a binary mixture need not have the same effect as the addition of the same to a simple liquid. Thus the addition of sodium carbonate raises the boiling point of water, but depresses the boiling point of mixtures of water and alcohol, provided that the amount of alcohol exceeds a certain limit.

J. C. P.

Rendering Passive, Passivity, and Rendering Active of Iron. By HENRY L. HEATHCOTE (*Zeit. physikal. Chem.*, 1901, 37, 368—373).—Drawn iron immersed in nitric acid of sp. gr. 1.40 becomes passive, but invariably some of the iron is dissolved. Nitric acid of lower sp. gr., 1.25, can also render iron passive. Electrolytically deposited iron is very quickly made passive in acid of sp. gr. 1.40; and slightly oxidised iron in acid of sp. gr. 1.3 also becomes passive.

Iron maintains its passive state (independently of the method by which this has been brought about) for a considerable time in strong nitric acid; it is, however, slowly dissolved.

The rate at which iron is rendered active in dilute nitric acid is accelerated by stirring, which indicates that this process is of the nature of a solution phenomenon. In a concentrated solution of potassium nitrate, passive iron becomes active in a few seconds; in 2*N* potassium hydroxide solution, the passivity remains for 2—3 minutes, whilst in saturated solutions of potassium dichromate or iron alum the iron may still be passive after several days. Passive iron may be dried and even placed under diminished pressure (7—8 mm.) without becoming active. The *E.M.F.* of a cell consisting of: passive iron | dilute sulphuric acid | iron: shows a gradual fall of potential until about 0.89 volt is reached, when it remains stationary for a moment, then steadily continues to fall. When a current was passed through

the cell, platinum⁺ | nitric acid of sp. gr. 1.4 | iron⁻, the needle of the ammeter showed regular oscillations, and the cathode had the appearance of iron dissolved pulsation-wise.

Iron periodically dissolved has a characteristic appearance; the surface is smooth and eaten out at places.

A long rod of passive iron immersed in nitric acid (1.315*N*), when touched under the liquid with zinc, forms an active zone which propagates itself along the rod, continually diminishing in size until it

ultimately disappears and leaves the whole passive. A piece of dry passive iron, when touched with glass or zinc, becomes active only at the spot touched.

The author concludes that the passive state is not due to protection by a film either of liquid or of gas. The passivity of iron does not spontaneously disappear, but only when it is subject to some external exciting influence.

J. McC.

Inorganic Chemistry.

Solubility of Gases in Water. III. By LUDWIG W. WINKLER (*Ber.*, 1901, **34**, 1408—1422. Compare Abstr., 1891, 384; 1892, 271).—From data previously obtained (*loc. cit.*) for the solubility of nitrogen and oxygen in water, the absorption coefficient of air at temperatures between 0° and 100° is calculated; its value is 0·02881, 0·02264, 0·01869 at 0°, 10°, and 20° respectively—numbers which are rather larger than those calculated by Bunsen from the solubility of nitrogen and the composition of the air obtained by boiling out water. A table is given showing the volume of air absorbed by 1000 c.c. of water at all temperatures between 0° and 100°. The percentage of oxygen in the air obtained by boiling out water diminishes as the temperature of absorption rises, and may be calculated by the equation, $n = 35·47 - 0·0338t$, where n is the percentage of oxygen and t is the temperature.

The author has also determined the absorption coefficients of nitric oxide, carbon monoxide, methane, and ethane. The following table shows within what limits the values lie :

| | Absorption coefficient. | |
|------------------------|-------------------------|---------|
| | At 0°. | At 80°. |
| Nitric oxide..... | 0·07381 | 0·02700 |
| Carbon monoxide | 0·03537 | 0·01430 |
| Methane | 0·05563 | 0·01770 |
| Ethane | 0·09874 | 0·01826 |

In the case of carbon monoxide and ethane, the values at the ordinary temperature are higher, in the case of methane lower, than those given by Bunsen. Nitric oxide and carbon monoxide were found to have a slight chemical action on water, and a corresponding correction was introduced in the author's calculations. J. C. P.

Iodine and the Colour of Iodine Solutions. By WILHELM VAUBEL (*J. pr. Chem.*, 1901, [ii], **63**, 381—384).—Solutions of iodine may be divided into two classes, violet solutions, which transmit red and blue light as does iodine vapour, and yellow or brown solutions, which transmit no blue light, but only red, yellow, and green. The solvents of the first class are carbon disulphide, hydrocarbons, and their halogen derivatives, and other halogen containing substances.

Those of the second class are oxygen and nitrogen compounds, alcohols, aldehydes, ketones, ethers, and acids, provided they do not contain halogen. It is noteworthy that a solution in 83 per cent. sulphuric acid is violet, which on dilution to about 66 per cent. becomes yellow.

K. J. P. O.

Simple method for obtaining a Saturated Aqueous Solution of Hydrogen Sulphide or a Constant Supply of the Gas. By F. MOLLWO PERKIN (*J. Soc. Chem. Ind.*, 1901, 20, 438).—The apparatus (of which a figure is given) is so arranged that the space above the liquid in the bottle containing the aqueous solution is always filled with an atmosphere of the gas, which is renewed automatically by a constant generator when either the solution is drawn out for use or the gas allowed to escape. The solution is thus protected from oxidation, and is maintained in a saturated condition.

M. J. S.

Action of Anhydrous Sulphuric Acid on dry Potassium Persulphate. By A. BACH (*Ber.*, 1901, 34, 1520—1522).—The experiments described in a former paper (this vol., ii, 14), were repeated, care being taken to exclude water by using 100 per cent. sulphuric acid throughout, and employing carefully dried potassium persulphate and permanganate; similar results, however, were obtained as before, 1.31 times the calculated volume of oxygen being evolved. This corresponds with a conversion of 5/8 of the active oxygen of the persulphate into a "higher persulphuric acid" and of 3/8 into a simple acid, and shows that small quantities of water do not affect the formation of the higher acid, or its decomposition by manganese heptoxide. It is noteworthy that in the anhydrous solution, potassium persulphate gives the titanous acid reaction for hydrogen peroxide, although the latter cannot, under the conditions, be present.

W. A. D.

Preparation of large quantities of Tellurium. By EDWARD MATTHEY (*Proc. Roy. Soc.*, 1901, 68, 161—163).—In obtaining bismuth from its ores, tellurium, if present, must be removed. Treating the alkaline residues containing the tellurium by acidification with hydrochloric acid and precipitation with sodium sulphite, the author has obtained 57½ lbs. of tellurium from 321 tons of ore, the latter containing, on the average, 22.5 per cent. of bismuth. The tellurium has a sp. gr. 6.27; the temperature of solidification is 450°, and the electrical resistance is about 800 times that of copper, but depends largely on the crystalline conditions; the thermo-electric power of tellurium appears to be great.

J. C. P.

Some Physical Properties of Nitric Acid Solutions. By VICTOR H. VELEY and J. J. MANLEY (*Proc. Roy. Soc.*, 1901, 68, 128—129. Compare *Abstr.*, 1898, ii, 277).—The properties examined are the densities, with special reference to the contractions, and the refractive indices. The investigation shows that the physical properties are discontinuous only at points corresponding with simple molecular proportions of nitric acid and water; the best defined points, indicated either by the density or by the refractive index, or by both, are those corresponding with the hydrates with 14, 7, 4, 3, 1.5, and 1 H₂O. A remarkable discontinuity is indicated at concentrations between 95 and

100 per cent., in agreement with the authors' previous determination of the electrical conductivity (*loc. cit.*); possibly this discontinuity may be explained otherwise than by the combination of acid and water. The contractions show that the points of discontinuity are not absolutely sharp, as there is a transition stage, within the limits of 1—2 per cent., in the vicinity of such points.

The specific refraction, calculated both by Gladstone and Dale's, and by Lorentz's formula, decreases with increasing concentration. Pulfrich's formula, expressing the relation between the refractive index and the contraction in terms of a constant, is approximately applicable, but that only for neighbouring concentrations.

J. C. P.

Volatility of Boric Acid in Steam. By FREDERICK W. SKIRROW (*Zeit. physikal. Chem.*, 1901, 37, 84—90).—A large number of unsaturated boric acid solutions have been distilled and the concentration of the acid in the distilling liquid and in the distillate determined. It is found that as the former concentration increases, the latter increases also, but more slowly. On the hypothesis that only one of the hydrates, H_3BO_3 , $\text{H}_2\text{B}_4\text{O}_7$, $\text{H}_2\text{B}_2\text{O}_4$, is volatile, it follows from the results that H_3BO_3 is the volatile form. The lowering of the vapour pressure, however, is less than is in accordance with the above hypothesis, and the author finds that the other hydrates are increasingly formed in the solution with rising concentration. The two following equations would express the equilibria: (1) $4\text{H}_3\text{BO}_3 \rightleftharpoons 5\text{H}_2\text{O} + \text{H}_2\text{B}_4\text{O}_7$; (2) $2\text{H}_3\text{BO}_3 \rightleftharpoons 2\text{H}_2\text{O} + \text{H}_2\text{B}_2\text{O}_4$. The ratio of the H_3BO_3 concentrations in solution and vapour is calculated to be 2.2×10^5 .

J. C. P.

Reduction of Silver Chloride by Hydrogen and the Inverse Reaction. By JOUNIAUX (*Compt. rend.*, 1901, 132, 1270—1272).—Above 600° , the conditions of equilibrium are the same whether the original system consisted of silver and hydrogen chloride or of silver chloride and hydrogen, and the proportion of hydrogen chloride increases with the temperature, and amounts to 95 per cent. at 700° . The value of p is higher the lower the pressure in the tube, both at 540° and at 640° . The experimental values for the conditions of equilibrium agree closely with those calculated from thermodynamical formulæ.

MARCELLIN P. E. BERTHELOT (*ibid.*, 1273) points out that when silver is heated in hydrogen at about 550° , it disintegrates, and undergoes changes in molecular condition with possibly the formation of a hydride, and these changes must be taken into account when considering the conditions of equilibrium of any reaction in which it takes part at high temperatures.

C. H. B.

Reducing Power of Calcium Carbide. By FR. VON KÜGELGEN (*Zeit. Elektrochem.*, 1901, 7, 541—550, 557—568, and 573—580).—When a mixture of lead oxide and calcium carbide is heated, reaction takes place at a comparatively low temperature, the mass becoming red hot. To complete the reaction, it is necessary to heat the mixture to a dull red heat. When the theoretical quantity of calcium carbide

is used, the gas evolved consists entirely of carbon dioxide ; with larger quantities of carbide, small quantities of carbon monoxide are also present (compare this vol., ii, 98). Quantitative experiments show that the principal reaction is represented by the equation $5\text{PbO} + \text{CaC}_2 = 5\text{Pb} + \text{CaO} + 2\text{CO}_2$. The change appears, however, to take place in two stages, the first of which is complete at a lower temperature than the second ; they correspond with the equations (1) $\text{PbO} + \text{CaC}_2 = \text{Pb} + \text{CaO} + 2\text{C}$ and (2) $4\text{PbO} + 2\text{C} = 4\text{Pb} + 2\text{CO}_2$. The lead obtained contains traces of calcium ; when calcium chloride was used as a flux and to prevent oxidation, the lead contained from 0.06 to 0.08 per cent. of calcium ; in absence of calcium chloride, 0.12 to 0.2 per cent., according to the excess of calcium carbide employed.

A mixture of lead chloride and calcium carbide undergoes the change $\text{PbCl}_2 + \text{CaC}_2 = \text{CaCl}_2 + \text{Pb} + 2\text{C}$ when it is heated. The reaction may be started by applying the flame of a match to one part of the mixture, it then spreads with almost explosive violence through the whole mass. The carbon which is separated prevents the union of the lead particles to a regulus.

A mixture of lead chloride and lead oxide gives a better result, the high temperature produced by the reaction of the lead chloride and calcium carbide causing the lead oxide and carbon to react. A mixture containing the quantities required by the equation $\text{PbCl}_2 + 4\text{PbO} + \text{CaC}_2 = 5\text{Pb} + \text{CaCl}_2 + 2\text{CO}_2$ could not be ignited, even by a core of the mixture of lead chloride and calcium carbide, a mixture of lead chloride (150 parts), lead oxide (120), and calcium carbide (39.24), however, evolved enough heat to fuse the whole mass, leaving a regulus of 200 parts of lead. The reactions occurring in this case are $\text{PbCl}_2 + \text{CaC}_2 = \text{Pb} + \text{CaCl}_2 + 2\text{C}$ and $4\text{PbO} + \text{C}_2 = 4\text{Pb} + 2\text{CO}_2$.

The results obtained with copper oxide and chloride are very similar to those obtained with the corresponding lead compounds. Copper oxide and calcium carbide react first at about the melting point of silver ; the reaction is then very violent. In presence of calcium chloride, the metal contains 0.036 to 0.124 per cent. of calcium ; by using a large excess of calcium carbide and no flux, copper containing 1.06 per cent. of calcium was obtained. The reaction between copper chloride and calcium carbide is quite similar to that between lead chloride and calcium carbide, but it is more violent. Owing to this circumstance, a mixture of copper chloride, copper oxide, and calcium carbide in the proportion $\text{CuCl}_2 + 4\text{CuO} + \text{CaC}_2$ reacts with great rapidity when ignited with a match.

The temperature produced by the reaction of copper chloride and calcium carbide is sufficiently high to bring about the reduction of other oxides by the carbon which is formed. The following results were obtained :

| Mixture heated. | Composition of alloy formed. |
|--|------------------------------------|
| CuCl_2 (5) ; ZnO (5) ; CaC_2 (3). | Cu, 86.4 ; Zn, 13.48 ; Ca, 0.041. |
| CuCl_2 (5) ; SnO_2 (11.65) ; CaC_2 (2.71). | Cu, 24.47 ; Sn, 74.84 ; Ca, 0.037. |
| CuCl_2 (5) ; Mn_2O_3 (5) ; CuO (5) ; CaC_2 (3). | Cu, 91.02 ; Mn, 8.88 ; Ca, trace. |

An aluminium bronze could not be prepared in this way. A mixture

of silver chloride with about $1/4$ its weight of calcium carbide reacts quickly when ignited with a match, leaving a button of fused silver. Zinc oxide is reduced at a bright red heat, whilst a mixture of zinc chloride and calcium carbide may be ignited; the zinc produced is, however, in the form of a sponge or powder. From a mixture of zinc chloride, copper oxide, and calcium carbide, almost the whole of the zinc may be obtained as an alloy; this is not the case with the mixture of copper chloride and zinc oxide. By replacing some of the copper oxide in this mixture by nickel oxide, German silver is obtained.

Mercuric oxide and calomel are reduced by calcium carbide, the reactions being accompanied by comparatively small development of heat.

Stannic oxide is reduced incompletely at a bright red heat; with stannous chloride, the reaction does not require external heat, but the tin remains mixed with the slag as a powder. A mixture of the chloride and oxide gives a somewhat better result. A mixture of stannous chloride and copper oxide is very readily reduced by calcium carbide. Arsenious oxide is reduced at a dull red heat. Bismuth oxide, chloride, or oxychloride are readily reduced to the metal without the aid of external heat. Chromic oxide is very incompletely reduced at a bright red heat, chromic chloride reacts without external heat; in both cases, the metal is in the form of powder, and in the second it contains carbon. Molybdic and tungstic acids are reduced at high temperatures, yielding metallic powders. Manganese compounds behave like those of chromium; manganese bronze was, however, readily obtained by heating a mixture of manganese chloride (10 parts), copper oxide (12.1), and calcium carbide (5.78) to a bright red heat with calcium chloride as flux. The bronze contained 10.71 per cent. Mn, 89.36 per cent. Cu, and 0.04 per cent. Ca. Ferric oxide is incompletely reduced at a high temperature; ferric chloride reacts without external heat, yielding a powder of iron. Nickel compounds behave similarly. Potassium and sodium hydroxides are reduced at comparatively low temperatures, hydrogen and carbon monoxide being formed in addition to calcium oxide, metallic sodium, or potassium and their carbonates. Metallic sodium is also formed when sodium chloride is fused with calcium carbide; in presence of lead, it can be isolated in the form of the lead alloy. Magnesium could not be isolated, although the chloride appears to be reduced by calcium carbide. Aluminium oxide is incompletely reduced, the chloride reacts without external heat, yielding a powder mixed with much carbon; in presence of finely divided copper, an alloy containing 2.59 per cent. aluminium was obtained in small quantity. Cerium oxide was not reduced; the chloride yielded some cerium carbide in the form of powder.

T. E.

Magnesium Nitride. By W. KIRCHNER (*Chem. Zeit.*, 1901, 25, 395. Compare Eidmann and Moeser, this vol., ii, 240).—Long, thin magnesium turnings are formed into a coherent mass by being pressed and well hammered in a hollow iron cylinder, and are then ignited by applying a light. The product consists of a solid core of greenish-yellow magnesium nitride with a thin crust of oxide which can readily be removed.

J J. S.

Rate of Solution of Zinc in Acids. By T. ERICSON-AURÉN (*Zeit. anorg. Chem.*, 1901, 27, 209—253).—The solution of zinc in very dilute acids takes place in two periods; during the first, or induction period, the surface of the zinc becomes covered with bubbles of hydrogen which prevent the contact of the acid with the metal, and, consequently, a relatively small quantity of zinc is dissolved; during the second, or solution-period, the rate of solution gradually increases to a maximum, remains constant for some time, and then gradually decreases. The point at which this maximum is reached is independent of small differences of temperature, but with large variations in the temperature is reached sooner at lower than at higher temperatures. The presence of chlorides in large quantities also causes the maximum to be reached earlier. The rate of solution is determined by local electric circuits and by the direct chemical action of the acid on the zinc, and variations in the composition of the solution either increase or decrease the rate of solution according to their influence on these two phenomena.

At increasing concentrations, the rate of solution in hydrochloric and sulphuric acids is not proportional to the electrical conductivity of the acid, but increases more rapidly, and this increase is proportionally greater for hydrochloric than for sulphuric acid.

The influence of temperature on the rate of solution increases with the concentration of the acid, and with very dilute acid is not appreciable.

Non-electrolytes decrease the rate of solution; the decrease, however, is not proportional to the amount present, but is much greater proportionally for small quantities than for large quantities. In a given acid solution, the presence of an equal number of molecules of different non-electrolytes decreases the rate of solution in an equal degree.

The addition of small quantities of electrolytes (salts) to the acid decreases the rate of solution; on the further addition of the salt, the rate of solution is increased. On the continued addition of a salt, only those salts which produce a maximum electrical conductivity of the solution produce a maximum rate of solution of the zinc.

E. C. R.

Lead Suboxide. By SIMEON M. TANATAR (*Zeit. anorg. Chem.*, 1901, 27, 304—307).—Lead suboxide is obtained by decomposing lead oxalate at as low a temperature as possible in a current of carbon dioxide or nitrogen. It is a greyish-black powder of sp. gr. 8·342 at 18°, is not altered by dry air or by water, and is decomposed into lead oxide and lead by dilute acids and alkalis. One gram-mol. dissolved in acetic acid liberates 10 048 Cal., and since the solution of lead oxide in acetic acid liberates 15·500 Cal., the decomposition of lead suboxide into lead and lead oxide requires 5·452 Cal.

E. C. R.

Specific Gravity of Cuprous Iodide. By WALTHER SPRING (*Rec. Trav. Chim.*, 1901, 20, 79—80).—The sp. gr. of dry cuprous iodide is 5·653° at 15°, not 4·41° as stated by Schiff (*Annalen*, 1858, 108, 24); the molecular volume is thus 33·61, and is less than the sum of the atomic volumes of the elements (34·73), showing that, as usual, a contraction has occurred in combination.

W. A. D.

Crystallisation of Copper Sulphate. By ARTHUR J. HOPKINS (*Amer. Chem. J.*, 1901, 25, 413—419).—A discussion of the general conditions which determine the size of crystals, together with a method for the preparation of crystals of copper sulphate of any desired size. Preliminary experiments showed that neither concentration alone, nor the relation of the size of the dish to the volume of the solution, nor the rapidity of cooling, determines the size of the crystals, but that, for a given volume, concentration, and size of dish, it depends on the number of crystal points first started in the solution as it cools beyond the point of saturation. The method for starting any required number of crystal points is as follows. The hot measured solution (containing a little sulphuric acid) is poured into the crystallising dish, which is then carefully covered; it is left for 8—10 minutes to cool, a blast of air, under a pressure equivalent to 12 mm. of mercury, is blown upon the surface, and the latter is watched closely for the first minute crystals which appear. When the proper number of these crystals for the particular volume and concentration is not only formed but persists in the hot solution, the blast is removed and the crystals are left to grow. The mother liquor may be concentrated to the strength of the original solution, and another crop of crystals obtained in the same way. By this means, the author was able to obtain crystals of copper sulphate of 20—30 mm. in length.

E. G.

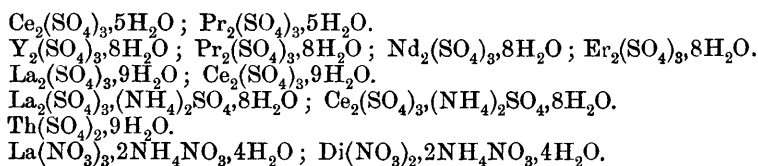
Action of Mercuric Oxide on Aqueous Solutions of Metallic Salts. By A. MAILHE (*Compt. rend.*, 1901, 132, 1273—1275).—The author has investigated the action of mercuric oxide at the ordinary temperature on solutions of certain metallic salts, and has obtained results different from those described by Rose (*Ann. Phys. Chem.*, 1859, 107, 298). Zinc chloride yields a white, crystalline oxychloride, $\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 3\text{H}_2\text{O}$, whilst the bromide yields a basic double salt, $\text{HgBr}_2 \cdot \text{ZnO} \cdot 8\text{H}_2\text{O}$, in long, monoclinic prisms. Zinc nitrate yields a microcrystalline product, $\text{Hg}(\text{NO}_3)_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$. Nickel chloride yields a green oxychloride, $\text{HgCl}_2 \cdot \text{NiCl}_2 \cdot 7\text{NiO} \cdot 10\text{H}_2\text{O}$, and the nitrate a compound, $2\text{Hg}(\text{NO}_3)_2 \cdot 3\text{NiO} \cdot 8\text{H}_2\text{O}$, which crystallises in hexagonal lamellæ. Cobalt chloride yields quadrangular plates of the composition $2\text{HgCl}_2 \cdot 6\text{CoO} \cdot \text{H}_2\text{O}$, and the nitrate yields red, monoclinic prisms of the compound $\text{Hg}(\text{NO}_3)_2 \cdot \text{CoO} \cdot 3\text{H}_2\text{O}$. Cupric chloride yields the amorphous oxychloride, $\text{CuCl}_2 \cdot 3\text{CuO} \cdot 4\text{H}_2\text{O}$, whilst the bromide yields green, quadrangular plates of the basic salt $\text{HgBr}_2 \cdot \text{CuO} \cdot 3\text{H}_2\text{O}$, and the nitrate, blue quadrangular prisms of the compound $\text{Hg}(\text{NO}_3)_2 \cdot \text{CuO} \cdot 4\text{H}_2\text{O}$. All these basic nitrates are somewhat readily decomposed by water. Copper sulphate solution has a slight action on mercuric oxide, but the other sulphates, as Rose stated, have no action.

C. H. B.

Mercurous Nitrite. By PRAFULLA CHANDRA RAY (*Annalen*, 1901, 316, 250—256. Compare *Trans.*, 1897, 77, 338; *Proc.*, 1896, 12, 218; 1899, 15, 103).—Mercurous nitrite is best prepared by digesting mercury with cold dilute nitric acid of sp. gr. 1.041, and purified by dissolving in hot water and crystallising from this medium.

G. T. M.

Some Salts of the Rare Earths. By E. H. KRAUS (*Zeit. Kryst. Min.*, 1901, 34, 397—431; and *Inaug. Diss. München*).—Previous crystallographic determinations made on salts of the rare earths are not in close agreement, since, on account of the imperfect methods of separation, the material examined was not quite pure. Detailed crystallographic, optical, and sp. gr. determinations are now given of the following salts, mainly hydrated sulphates, and the calculated topic axial ratios are compared :



L. J. S.

Density of Alloys. By EDMOND VAN AUBEL (*Compt. rend.*, 1901, 132, 1266—1267).—An aluminium-antimony alloy, the composition of which corresponds with that required for the formula AlSb , melts at 1078—1080°, although aluminium and antimony melt respectively at 660° and 630°. The sp. gr. of this alloy is 4.2176 at 16°/4°, whereas the sp. gr. calculated from the composition is 5.2246. It follows that the formation of the alloy is accompanied by a relatively very large increase in volume, 7.07 c.c. of aluminium and 12.07 c.c. of antimony yielding 23.71 c.c. of alloy.

C. H. B.

Hydrated Chromium Chlorides. By ALFRED WERNER and AL. GUBSER (*Ber.*, 1901, 34, 1579—1604. Compare Recoura, *Abstr.*, 1886, 508; Marchetti, 1893, ii, 122; Piccini, 1895, ii, 229; Rohland, 1899, ii, 599).—Four definite hydrates exist: the isomeric green and greyish-blue salts containing $6\text{H}_2\text{O}$, and the compounds $\text{CrCl}_3 \cdot 10\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$. The greyish-blue hydrate corresponds with the compound $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$; it gives a purple coloured solution, the electrical conductivity of which remains practically constant, and at 25° is 324.5 for μ_{25} . All the chlorine is precipitated by silver nitrate, and its aqueous solution contains four ions, probably $\text{Cr}(\text{OH}_2)_6$ and 3Cl . A freshly prepared solution of the isomeric green salt has a conductivity at 25° and μ_{125} of 126, but after some 50 minutes this has increased to 236, and it continues to rise slowly until it reaches practically the same value as that of the greyish-blue salt; corresponding with the change in conductivity, a change in colour is observable. At 0°, the conductivity is 50 for μ_{125} , and changes but slowly. In aqueous solution, it appears to dissociate into two ions, probably $\text{CrCl}_2(\text{OH}_2)_4$ and Cl , as practically only one-third of the total chlorine is precipitated by silver nitrate at 0°. Two of the six mols. of water are less closely combined than the remaining four, and are readily removed when the green hexahydrate is kept in a desiccator; the product formed, $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$, resembles the original salt in properties, and only one of the three chlorine atoms is precipitated by silver nitrate. The constitution ascribed to the green hexahydrate is $\text{CrCl}_2(\text{OH}_2)_4 \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$, and corresponds with that of the double salt of Boltwood (*Zeit. anorg. Chem.*, 1895,

10, 181); for example, $\text{CrCl}_2(\text{OH}_2)_4\text{Cl}\cdot 2\text{CsCl}$. Red compounds, $\text{CrCl}_5(\text{OH}_2)\text{Rb}_2$ and $\text{CrCl}_5(\text{OH}_2)\text{Li}_2\cdot 2\text{H}_2\text{O}$, have also been prepared.
J. J. S.

Molybdenum Semipentoxide. By IVAR NORDENSKJÖLD (*Ber.*, 1901, 34, 1572—1577. Compare Klason, this vol., ii, 162).—The following salts have been prepared by methods similar to that employed by Klason.

Potassium molybdanyl chloride, $\text{MoOCl}_3\cdot 2\text{KCl}\cdot 2\text{H}_2\text{O}$, forms dark green, rhombic prisms; the *rubidium* salt, $\text{MoOCl}_3\cdot 2\text{RbCl}$, green, rhombic octahedra; the *caesium* salt, $\text{MoOCl}_3\cdot 2\text{CsCl}$, yellowish-green, rhombic octahedra. Similar compounds have been obtained with the hydrochlorides of methylamine, di- and tri-methylamine, ethylamine, di- and tri-ethylamine, and pyridine.

According to the author, Blomstrand's green oxychloride (*Annalen*, 1880, 201, 126) is a mixture of the pentachloride, MoCl_5 , with the oxychloride, MoO_2Cl_2 , in varying proportions.
J. J. S.

Isomorphism between the Salts of Bismuth and the Rare Earths. By GÖSTE BODMAN (*Zeit. anorg. Chem.*, 1901, 27, 254—279. Compare Abstr., 1898, ii, 435).—The ratio of the specific volumes to the specific weights of mixed crystals of the nitrate and sulphate of bismuth, and of didymium, yttrium, and lanthanum, is in accordance with the view that they are isomorphous.
E. C. R.

Formation of Platinum Tetrachloride from Aqueous Hydrochloric Acid by Atmospheric Oxidation in contact with Platinum Black. By JOHN W. MALLETT (*Amer. Chem. J.*, 1901, 25, 430).—Platinum black, prepared by reducing a solution of the tetrachloride with formaldehyde, was washed with water and then left on the filter for several hours; on the addition of hydrochloric acid to the partially dried mass, a considerable quantity of it was dissolved, owing to oxidation of the hydrochloric acid by the occluded oxygen.
E. G.

Mineralogical Chemistry.

[Gold, &c., from Western Australia.] By EDWARD S. SIMPSON (*Ann. Rept. Geol. Survey Western Australia* for 1899, 1900, 48—55).—Several assays are given of native gold from various localities in Western Australia; they vary from Au 76·81, Ag 23·04, copper and iron 0·15 per cent. to Au 99·91, Ag 0·09. The latter, from Boulder, East Coolgardie, is of spongy gold, derived by the oxidation of gold telluride, and is even purer than the gold of Mount Morgan, in Queensland. The occurrence of native tin is noted in the stanniferous gravels at Greenbushes, and further information is given of stibiotantalite (*Trans.*, 1893, 63, 1076) from the same locality. The report also includes several analyses of mineral waters.

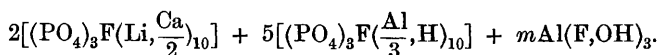
L. J. S.

Composition of Amblygonite. By HENRI LASNE (*Compt. rend.*, 1901, 132, 1191—1194).—The following new analyses are given of amblygonite from Montebraz (Creuse). I, of slightly translucent, faint greyish-pink material. II, of white, opaque material.

| | P ₂ O ₅ . | F. | H ₂ O. | Al ₂ O ₃ . | Li ₂ O. | Na ₂ O. | K ₂ O. |
|-----|---------------------------------|------|-------------------|----------------------------------|--------------------|--------------------|-------------------|
| I. | 46·85 | 8·51 | 3·00 | 34·01 | 8·50 | 1·00 | 0·18 |
| II. | 44·62 | 4·08 | 7·59 | 34·32 | 7·10 | 2·81 | 0·23 |

| | CaO. | FeO. | MnO. | Insol. | Total less O for F. |
|-----|------|------|------|--------|---------------------|
| I. | 0·23 | 0·76 | 0·13 | 0·55 | 100·15 |
| II. | 0·29 | 0·46 | 0·28 | 0·22 | 100·28 |

The formula is deduced as



In I, the value of m is 5, and in II it is 8. [The analyses, however, agree sufficiently closely with Penfield's simple formula, $\text{Li}(\text{AlF})\text{PO}_4$, in which lithium is partly replaced by sodium, &c., and fluorine by hydroxyl.]

L. J. S.

Thomsonite and Mesolite from Golden, Colorado. By HORACE B. PATTON (*Bull. Geol. Soc. Amer.*, 1900, 11, 461—474).—A description, illustrated by seven plates, is given of the several zeolites from the North and South Table Mountains, at Golden, Colorado. Several types of thomsonite are distinguished. The following analyses by R. Chauvenet and R. N. Hartmann are given. I, Freely projecting needles and prisms of thomsonite. II, Material from the centre of a radiating hemispherical mass of thomsonite. III, Fine cotton-like mesolite.

| | SiO ₂ . | Al ₂ O ₃ . | CaO. | Na ₂ O. | H ₂ O. | Total. |
|------|--------------------|----------------------------------|-------|--------------------|-------------------|--------|
| I. | 41·34 | 30·35 | 11·20 | 5·04 | 12·27 | 100·20 |
| II. | 41·59 | 30·59 | 11·15 | 4·66 | 12·24 | 100·23 |
| III. | 45·59 | 25·18 | 8·93 | 7·65 | 12·67 | 100·02 |

L. J. S.

Anorthite Crystals from Franklin Furnace, New Jersey. By CHARLES HYDE WARREN (*Amer. J. Sci.*, 1901, [iv], 11, 369—373).—Dull gray, tabular crystals of anorthite occur embedded in a white, crystalline limestone, near the contact of the latter with granite, at Franklin Furnace, New Jersey. A crystallographic description is given; the angle of optical extinction on (001) is -40° . The crystals enclose calcite, scales of graphite, and water. Analysis gave,

| SiO ₂ . | Al ₂ O ₃ . | CaO. | Na ₂ O. | CaCO ₃ . | H ₂ O. | Graphite. | Total. |
|--------------------|----------------------------------|-------|--------------------|---------------------|-------------------|-----------|---------|
| 40·16 | 34·89 | 18·26 | trace | 5·30 | 1·69 | 0·18 | 100·48. |

Crystallographic descriptions are also given of feldspar from Cripple Creek, Colorado, of wolframite from South Dakota, and of pseudomorphs of wolframite after scheelite from Trumbull, Connecticut. The wolframite from South Dakota is of interest in that it contains no manganese.

L. J. S.

Monchiquite from Mount Girnar, India. By JOHN WILLIAM EVANS (*Quart. Journ. Geol. Soc.*, 1901, 57, 38—53).—The monchiquite described is a fine-grained, black rock with numerous white specks, occurring, associated with nepheline-syenite, at Mount Girnar, Junagarh, Kathiawar. Under the microscope, it shows brown hornblende and green augite in a colourless, isotropic ground mass. The latter shows indications of crystalline structure and has a low index of refraction; it gelatinises with acids, and has a sp. gr. of about 2·2; these characters together with the following composition prove this material to be analcite.

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | Na ₂ O(K ₂ O). | H ₂ O. |
|--------------------|----------------------------------|----------------------------------|------|--------------------------------------|-------------------|
| 52·79 | 21·60 | 1·96 | 0·66 | 14·80 | 8·19 |

The occurrence of analcite as a primary constituent of igneous rocks is discussed (compare Abstr., 1898, ii, 170). L. J. S.

Composition of a so-called Blood Rain from Sicily. By FERDINAND JEAN and J. BRUHAT (*Ann. Chim. anal. appl.*, 1901, 6, 161—162).—The dust, which was of a pale ochre colour, was composed of moisture 0·974, organic substances 9·740, sodium and potassium chlorides and sulphates 1·948, iron, calcium and magnesium carbonates 23·051, iron and aluminium oxides 4·543 and silica 59·732; the small quantity of the sample at disposal prevented a more detailed analysis.

A microscopic examination showed very small and differently shaped fragments of silica; amorphous matters soluble with effervescence in dilute hydrochloric acid; vegetable *débris* (woody fibres, vegetable cells, fragments of mycelium, spores of mushrooms, circular spores of *Aspergillus* and oval spores of *Penicillium*); differently shaped fragments of diatoms; finally, small irregular polyhedrons coloured blue by iodine. Inoculated on gelatin, an abundant cultivation of *Aspergillus* was obtained. The authors are of opinion that the dust is not of volcanic origin but resembles that met with in the Sahara.

L. DE K.

Variation in the composition of Natural Mineral Waters detected by the aid of the Electrical Conductivity. By PAUL TH. MULLER (*Compt. rend.*, 1901, 132, 1046—1047).—The determination of the electrical conductivity of the water from a given spring affords a rapid method of ascertaining the secular variation in its composition and may also be applied in ascertaining whether samples of water from neighbouring sources have a common origin. The electrical conductivity of a natural water depends on the nature and amount of the dissolved electrolytes and in potable waters the substances present in solution are almost wholly of this nature.

G. T. M.

Physiological Chemistry.

Respiratory Quotient in Geese. By MAX BLEIBTREU (*Pflüger's Archiv*, 1901, 85, 345—400).—By feeding adult thin geese on food rich in carbohydrate, the respiratory quotient approaches unity. This depends on the increase of carbon dioxide discharged, not on a fall in the amount of oxygen consumed. The formation of fat from carbohydrate in the body must be associated with a splitting off of carbon dioxide.

The milky appearance of the blood-serum in such over-fed animals is due to finely emulsified fat. The origin of this fat is the food, for on starvation, or the giving of food free from fat, it disappears.

W. D. H.

Smallest amount of Oxygen in Water necessary to Fish Life. By JOSEF KÖNIG and B. HÜNNEMEIER (*Zeit. Nahr. Genussm.*, 1901, 4, 385—391).—Physiological experiments with gold-fish, carp, &c., duly recorded in tabular form. The investigation of this problem is beset with many difficulties, and as a rule the mortality among the fish is not merely due to want of oxygen, but to deleterious matters present in the waters.

It appears, however, that carp, which usually thrive in tranquil waters, become unwell if the amount of oxygen by volume is reduced to 0.4—0.1 per 100 c.c.

L. DE K.

Behaviour of Red Blood Corpuscles to certain Reagents. By GEORGE W. STEWART (*J. Physiol.*, 1901, 26, 470—496).—The difference in the behaviour of red blood corpuscles to ammonium chloride and sodium chloride is dependent on the structure of the corpuscle, and principally of the colourless portion of it (stroma, envelope, ghost). The difference is shown by blood which has stood for as much as 12 days without being laked, by blood fixed by formaldehyde, and to a less extent by blood laked by saponin and by water. The resistance to the entrance of ammonium chloride is, however, much greater for fresh than for stale corpuscles. Formaldehyde shortens this period of resistance, and even renders the corpuscles permeable to sodium chloride. Later on, the permeability for ammonium chloride diminishes and that for sodium chloride disappears.

Saponin and water have the same effect on the conductivity of the blood whether they are added to fresh blood, stale blood, blood hardened by formaldehyde, or blood laked by heat. This action does not depend on the liberation of blood pigment. When blood is laked by ammonium chloride or water after the corpuscles have been partially fixed by formaldehyde, the 'ghosts' retain the form of thin discs. Formaldehyde changes hæmoglobin into methæmoglobin.

W. D. H.

Gastric digestion in Elasmobranchs. By ERNST WEINLAND (*Zeit. Biol.*, 1901, 41, 275—294).—The pure gastric juice of the dogfish, torpedo, or ray is a clear, usually acid liquid. The acidity increases by feeding. No hydrochloric acid is present, but the acid is an organic one. The juice of the dogfish is slightly laevorotatory. In the secretion, and in the mucous membrane of the dogfish, is a proteolytic enzyme which acts more readily in an acid than in an alkaline medium. In the stomach of the ray is also probably a diastatic ferment which acts only in an alkaline medium; the alternation of acid and alkaline reaction in the gastric juice of this animal is thus useful.

W. D. H.

Effects of the increased consumption of Sugar. By GUSTAV VON BUNGE (*Zeit. Biol.*, 1901, 41, 155—166).—In addition to analyses of honey and fruits which the paper contains, the main point discussed is the influence of sugar as food on metabolism and growth. It is suggested that the anæmia and carious teeth attributed to sugar in the diet of children may be explained by the lessening of iron and calcium if sugar is substituted to any great extent for other articles of a child's food.

W. D. H.

Digestibility of Dextrose. By L. DUCLERT and R. SÉNÉQUIER (*Ann. Agron.*, 1901, 27, 209—220).—Small amounts of dextrose (10—25 grams) were completely absorbed by rabbits; even with 50 grams, none of the sugar passed into the urine or fæces. With 75 grams of dextrose, the gastric mucus and the mucus of the intestine were greatly altered. One hundred grams of dextrose caused the passage of urine and fæces to cease, whilst perforations were found in the stomach; both 75 and 100 grams caused the death of the rabbits.

Further experiments in which rabbits were fed with lucerne and dextrose showed that the presence of the latter did not affect the digestibility of the proteids.

N. H. J. M.

Intestinal absorption of Maltose. By E. WAYMOUTH REID (*J. Physiol.*, 1901, 26, 427—435).—The experiments recorded are similar to those previously described in connection with dextrose. In the normal intestine, the uptake of dextrose and maltose is independent of the relative rates of diffusibility of these substances, although when the epithelium is rendered inactive or removed, these substances leave the gut at the same relative rates as those at which they diffuse through parchment into serum. It is suggested that the ferment which converts maltose into dextrose is produced below the level of the attached ends of the epithelial cells.

W. D. H.

Effect of the withholding of Water on Metabolism. By ALBERT SPIEGLER (*Zeit. Biol.*, 1901, 41, 239—270).—The withholding of water from the diet for short periods produces a lessening of proteid decomposition. This is more marked in men than in dogs, and is explained by a lessening of proteid absorbed from the alimentary canal. In some cases, where apparently there is an increased amount

of digestive fluid secreted, the fall is hardly noticeable. If water is withheld for long periods, there is a rise in proteid katabolism. No evidence of retention in the body of the products of such decomposition was obtained.

W. D. H.

Proteid Katabolism in Inanition. By ERWIN VOIT (*Zeit. Biol.*, 1901, 41, 167—195).—A number of metabolism experiments on various animals in a state of inanition are described and compared with others previously recorded. The amount of proteid decomposition depends on the previous condition of the animals, particularly the amount of fat they contain, the amount of work, and other factors.

W. D. H.

Variations in the composition of the Bile. By R. L. CRACIUNU (*Compt. rend.*, 1901, 132, 1187—1189).—The bile of eighteen animals was analysed. In young animals, the solids are more abundant than in old ones. In thin animals, the solids are more abundant than in fat ones. The amounts of fat and lecithin in the bile increase with age.

W. D. H.

Secretion and composition of Human Bile. By J. BRAND (*Proc. K. Acad. Wetensch. Amsterdam*, 1901, 3, 584—585).—From the examination of the bile in nine cases of cholecystotomy, it is found that the secretion is continuous, sinking in the night, and showing two maxima in the day probably related to the taking of meals. The amount per diem may reach 1100 c.c. The concentration of the bile is fairly constant; the percentage of solids in free flowing bile may reach 1.41, and in that of the gall bladder 20. The amount of pigment (bilirubin, urobilin, and a very small amount of hæmatoporphyrin) is low. The proportion between taurocholate and glycocholate varies between 1.45 and 1.54. A small quantity of sulphur is in combination as ethereal sulphates. The molecular concentration of the bile, whether from the bile duct or gall bladder, is equal to that of blood; but the electrolytic conducting power is greater. It is surmised that mucin influences dissociation or is linked to inorganic compounds.

W. D. H.

Variations in the amount of Thiocyanate in Human Saliva By E. C. SCHNEIDER (*Amer. J. Physiol.*, 1901, 5, 274—280).—The thiocyanate in saliva was estimated in a large number of specimens by the methods of Munk and Solera-Krüger. In smokers, the average percentage of potassium thiocyanate is 0.013; in non-smokers, 0.003. The amount diminishes on prolonged stimulation of the salivary glands. The parotid saliva is always richer than the sub-maxillary saliva of the same person at the same time (compare Grober, this vol., ii, 402).

W. D. H.

Composition of Sweat. By WILLIAM CAMERER, jun. (*Zeit. Biol.*, 1901, 41, 271—274).—The following table gives the analyses of sweat obtained from a healthy adult man:

| | Light bath. | Hot air bath. | Steam bath. |
|--------------------------|--------------------------------|---------------|---------------|
| Quantity, in grams | 60—100 | 120 | 300 |
| Specific gravity | 1·0084 | 1·010 | 1·0055 |
| Reaction | { once acid once alkaline } | | acid alkaline |
| Water, per cent... | 97·9 | 98·3 | 99·24 |
| Ethereal extract „ ... | 0·17 | 0·02 | 0·08 |
| Total nitrogen „ ... | 0·15—0·19 | 0·137 | 0·09 |
| Urea nitrogen „ ... | 0·05 | — | 0·03 |
| Ammonia nitrogen „ ... | 0·012 | 0·011 | 0·006 |
| Ash „ ... | 0·86—1·04 | 1·04 | 0·46 |
| Sodium chloride „ ... | 0·66 | 0·78 | 0·34 |
| Proteid „ ... | trace | — | trace |

W. D. H.

Transport of Fluid by Epithelia. By E. WAYMOUTH REID (*J. Physiol.*, 1901, 26, 436—444).—Experiments are recorded with the ‘surviving’ intestinal mucous membrane of the rabbit, which show that the physiological transport of fluid by the epithelium, as described by Cohnheim, depends on the vitality of the cells; and in warm blooded animals, a low temperature of observation, and deficient oxygenation, rapidly produce death of the active cells. W. D. H.

Rigor Mortis and the Formation of *d*-Lactic Acid. By W. A. OSBORNE (*Proc. Physiol. Soc.*, 1901, xlix—l).—Lactic acid is estimated by preparing the barium salt in solution, heating this with excess of sulphuric acid, and weighing as barium sulphate.

The post mortem formation of lactic acid starts immediately the circulation ceases, and before the onset of rigor. *Rigor mortis* is retarded in mammalian muscle by a previous irrigation through the blood vessels of normal saline solution; the amount of acid formed is also less. If the circulation through a limb is stopped, and the muscles are stimulated either directly or indirectly, the amount of lactic acid formed is approximately equal to that found in the muscles of the opposite limb during *rigor*. If a 0·4 per cent. solution of sarco-lactic acid in normal saline solution is led through the hind limbs, the muscles contract spasmodically and pass into *rigor*. The spasms may be arrested and the muscles regain vitality by substituting an alkaline saline solution for the acid one at an early stage of the experiment. Acids other than lactic, however, produce the same result.

W. D. H.

Chemistry and Heat Rigor Curves of Voluntary and Involuntary Vertebrate Muscle. By SWALE VINCENT and THOMAS LEWIS (*J. Physiol.*, 1901, 26, 445—464).—*Rigor mortis* occurs in unstriated muscle, when it is kept some time at the body temperature; slight but definite acidity also occurs. Extracts of unstriated muscle are usually neutral or alkaline, whilst those of striated muscle are usually acid. The characteristic proteid or proteids are probably identical in both cases; the absence of paramyosinogen in fresh extracts of

unstripped muscle is probably due to the reaction. The heat-rigor curves of both kinds of muscle (Brodie's method) show the following contractions, one well marked at 47° — 50° , the next a small contraction at 56° , and a third again well marked at 63° ; the last is attributed to the contraction of connective tissue elements in the muscle. The curves of amphibian muscle show contractions at 38° — 40° , and 45° — 50° in the case of striped, and at 47° and 54° in the case of unstripped, muscle. After muscle has undergone *rigor mortis*, the only contraction is at 63° . Paramyosinogen and myosinogen are possibly formed from a common precursor present in living muscular tissue which coagulates at 47° . The three tissues, unstripped, cardiac, and striped muscle, form a descending series with regard to the amount of nucleo-proteid present; unstripped muscle contains about eight times as much as striped.

W. D. H.

Composition of Elastic Tissue. By G. W. VANDERGRIFT and WILLIAM J. GIES (*Amer. J. Physiol.*, 1901, 5, 287—297).—The *ligamentum nuchæ* of the calf contains 65.1 and of the ox 57.6 per cent. of water. The solids in the ligament from the ox are as follows in percentages:

Inorganic matter 1.1 (SO_3 , 0.062; P_2O_5 , 0.081; Cl, 0.32). Organic matter, 98.1.

| | |
|----------------------------|-------|
| Fat | 2.64 |
| Albumin and globulin | 1.45 |
| Mucin | 1.24 |
| Elastin..... | 74.64 |
| Gelatin..... | 17.04 |
| Extractives, &c. | 1.88 |

W. D. H.

Proteids of the Thymus. By W. HUISKAMP (*Zeit. physiol. Chem.*, 1901, 32, 145—197).—Nucleo-histon is the most abundant proteid in thymus; it comprises 69.4 per cent. of the total proteids; 18.7 per cent. of nucleo-proteid, and 11.9 per cent. of other proteids are present. The characters and composition of nucleo-histon and nucleo-proteid are fully described, together with their compounds with calcium, magnesium, and sodium. Nucleo-histon contains 3.7 and nucleo-proteid 0.9 per cent. of phosphorus. The influence of these proteids on the coagulation of blood plasma was found to be much the same as described by Hammarsten with solutions of fibrinogen.

W. D. H.

Thyreo-globulin. By AD. OSWALD (*Zeit. physiol. Chem.*, 1901, 32, 121—144).—Thyreo-globulin is the main constituent of the colloidal substance of the thyroid vesicles; the nucleo-proteid described by others probably comes, at any rate in part, from the cells. The composition of thyreo-globulin is pretty much the same in various animals, including man. It is the active material of thyroid extract, and contains iodine in combination. The amount of iodine varies considerably, it may even be absent; this is probably largely due to diet.

W. D. H.

Decomposition and Formation of Fat in the Tissues. By C. HESTER (*Virchow's Archiv*, 1901, 164, 293—343).—By local injection

of olive oil into muscles, it is shown that absorption of the fat occurs in the muscular fibres, the fascia cells, and the nerve sheaths. This is hindered by operative interference with the activity of the muscle, such as dividing its tendon. The application of such experiments to fatty degeneration of muscle and in Basedow's disease is pointed out. Further, decomposition of fat occurs in the tissue fluid, and synthesis of fat from the products of decomposition occurs in the muscular fibres. The first action is attributed to the lipase of the blood. W. D. H.

Proteolytic Enzymes in the Organs and Tissues of the Body. By SVEN G. HEDIN and S. ROWLAND (*Proc. Physiol. Soc.*, 1901, xlviii—xlix).—Enzymes were searched for in the expressed juice of certain organs. The amount of nitrogen not precipitable by tannic acid before and after digestion at blood heat in the presence of toluene was estimated. Proteolytic enzymes are present in the juice of lymphatic glands, liver, kidney, and spleen. These have about equal power; the spleen enzyme works best in an acid medium. Weaker enzymes, acting principally in acid solutions, were found in the heart and mammary gland. The enzyme of skeletal muscle is rather weak, and acts equally in acid and alkaline solutions. W. D. H.

[Properties and Composition of Glycogen.] By JOSEPH NERKING (*Pflüger's Archiv*, 1901, 85, 313—319, 320—329).—All the glycogen in muscle cannot be extracted by means of water; the remainder, which in three experiments amounted to 27.5, 33.1, and 16.6 per cent. respectively, can be extracted with dilute alkali.

Analysis of glycogen from the same source gave results which nearly correspond with those required for the empirical formula $C_6H_{10}O_5$.

By inversion with various acids, and for variable periods at the boiling point, it is shown that all the glycogen is not represented in the sugar obtained. The best results were obtained by heating with 2.2 per cent. hydrochloric acid for 3 hours. Here 97 per cent. was converted into sugar. The corresponding number with starch is 95. More prolonged heating leads to a loss of sugar. W. D. H.

Protamine from *Accipenser stellatus*. By D. KURAÉEFF (*Zeit. physiol. Chem.*, 1901, 32, 197—200).—Protamines were prepared from the testis of *Accipenser stellatus*, *Silurus glanis*, and the hake. The former only was obtained in sufficient amount for analysis, the formula of its sulphate being $C_{35}H_{72}O_9N_{18} \cdot 4H_2SO_4$. Examination of its decomposition products (hexon bases) show that the new protamine (*Accipenserine*) belongs to the sturine group. W. D. H.

The Red Colour of Salted Meat. By JOHN S. HALDANE (*J. Hyg.*, 1901, 1, 115—122).—The red colour of cooked salt meat is due to nitric oxide hæmochromogen; this pigment is produced by the decomposition by heat of nitric oxide hæmoglobin. The latter pigment is formed by the action of nitrites on hæmoglobin in the absence of oxygen and presence of reducing agents. The nitrites are formed by reduction within the raw meat from the nitre used in salting. The nitrite is destroyed by prolonged cooking. W. D. H.

Experiments on the Influence of Diet on the separation of Acetone. By SCHUMANN-LECLERQ (*Chem. Centr.*, 1901, i, 1113; from *Wien. klin. Woch.*, 14, 237—242).—Experiments *in persona* confirm the theory that the decomposition of fat in the organism is the main, if not the only, cause of the separation of acetone. The acetone is derived from the fat of the body or of the food in a state either of hunger or of repletion, and whether the diet is of fat or of flesh.

Carbohydrates tend to prevent the formation of acetone by protecting the labile fat before its oxidation.

E. W. W.

Excretion of Antipyrin. By D. LAWROFF (*Zeit. physiol. Chem.*, 1901, 32, 111—120).—Antipyrin is excreted in the urine as a compound of glucuronic acid.

W. D. H.

Chemistry of Nerve Degeneration. By FREDERICK W. MOTT and WILLIAM D. HALLIBURTON (*Proc. Roy. Soc.*, 1901, 68, 149—151. Compare this vol., ii, 260).—A fuller account of researches previously published. the following tabular summary gives the main facts in relation to the experiments on animals :

| Days after section. | Cats' sciatic nerves. | | | Condition of blood. | Condition of nerves. |
|---------------------|-----------------------|---------|-------------------------------------|--|--|
| | Water. | Solids. | Percentage of phosphorus in solids. | | |
| Normal ... | 65.1 | 34.9 | 1.1 | { Minimal traces of choline present. Choline more abundant. | { Nerves irritable and histologically healthy. Irritability lost ; degeneration beginning. |
| 1—3.. | 64.5 | 35.5 | 0.9 | | |
| 4—6..... | 69.3 | 30.7 | 0.9 | | |
| 8..... | 68.2 | 31.8 | 0.5 | { Choline abundant. | { Degeneration well shown by Marchi reaction. Marchi reaction still seen, but absorption of degenerated fat has set in. |
| 10..... | 70.7 | 29.3 | 0.3 | | |
| 13..... | 71.3 | 28.7 | 0.2 | | |
| 25—27..... | 72.1 | 27.9 | traces | { Choline much less. | { Absorption of fat practically complete. |
| 29.. | 72.5 | 27.5 | 0.0 | | |
| 44..... | 72.6 | 27.4 | 0.0 | { Choline almost disappeared. | { Return of function ; nerves regenerated. |
| 100—106... | 66.2 | 33.8 | 0.9 | | |

W. D. H.

Influence of Caffeine and Theobromine on the excretion of Purine substances in the Urine. By MARTIN KRÜGER and JULIUS SCHMID (*Zeit. physiol. Chem.*, 1901, 32, 104—110).—Caffeine and theobromine do not increase the excretion of uric acid.

The purine bases of the urine are, however, increased; 47 per cent. of the nitrogen of theobromine reappears in the urine as purine nitrogen.

W. D. H.

Inhalation of Ethylene. By J. LORRAIN SMITH and A. PERCY HOSKINS (*J. Hyg.*, 1901, 1, 123—124).—The opinion has been expressed by Roscoe in his evidence before the Water Gas Committee, 1899, that the poisonous action of coal gas and water gas is probably in part due to 'illuminant' hydrocarbons, of which ethylene is the chief, and not to carbon monoxide. Experiments on mice show that the poisonous effects are strictly proportional to the amount of carbon monoxide present. The effects produced by ethylene even when 72 per cent. of it are present are very slight. In air rendered poisonous by the addition of coal gas only about 0.2 per cent. of ethylene would be present, and so any toxic action due to ethylene is absent.

W. D. H.

[**Toxicity of Compounds containing both Cyano- and Hydroxyl Groups.**] By EDMOND FIQUET (*Bull. Soc. Chim.*, 1901, [iii], 25, 591—598).—See this vol., i, 469.

Behaviour of Cacodylic Acid in the Organism and its detection in Urine. By A. HEFFTER (*Chem. Centr.*, 1901, i, 1109; from *Schweiz. Woch. Pharm.*, 1901, 39, 193—195).—Cacodylic acid is decidedly less poisonous than arsenious acid. In the organism, a portion of the cacodylic acid is oxidised and arsenious or arsenic acid is separated in the urine, whilst the major portion is not attacked and passes into the urine unchanged. Several organs, especially the liver, stomach, and mucous membrane of the intestines, and to a less extent the muscles and kidneys, reduce the acid to cacodylic oxide. This reduction does not depend on the presence of living cells, but is brought about by an easily oxidisable substance, for an aqueous extract of liver has the same effect.

Cacodylic acid is estimated in urine by fusing [the residue left on evaporation?] with one part of potassium hydroxide and 3—4 of potassium nitrate, dissolving in hydrochloric acid, and precipitating the arsenic as sulphide.

E. W. W.

Artificial modifications of Toxins. By JAMES RITCHIE (*J. Hyg.*, 1901, 1, 125—144).—Tetanus toxin under the influence of hydrochloric acid readily loses its virulent properties, but the capacity of producing immunity remains. The less poisonous substances produced are probably toxoids. Sodium hydroxide or carbonate has similar power. Ricin is resistant to the action of hydrochloric acid, but when toxicity is destroyed, the capacity of producing immunity remains. Abrin is also resistant to the acid, but is relatively susceptible to sodium hydroxide; much the same is true for diphtheria toxin, although the power of producing immunity remains as in the other cases.

W. D. H.

Antidotes for chemically pure Proteids. By MANILLE IDE (*Chem. Centr.*, 1901, i, 1109; from *Fortschr. Med.*, 19, 234).—When rabbits are subjected to a prolonged treatment with pure proteids

from cow's milk, administered by injection, the serum is found to contain substances which experiments in glass vessels show to be capable of precipitating these proteids from solution. For the various proteids, such as pseudoglobulin and serum-albumins, different antidotes are formed, the action of each being limited to one proteid and to the same animal species. For every kind of cell there are as many antidotes as there are kinds of proteid contained in it. The agglutinins appear to be the antidotes for the proteids which are readily precipitated whilst the antitoxins correspond with the less easily precipitated substances.

E. W. W.

Chemistry of Vegetable Physiology and Agriculture.

Alcoholic Fermentation without Yeast Cells. X. By EDUARD BUCHNER and RUDOLF RAPP (*Ber.*, 1901, **34**, 1523—1530. Compare Abstr., 1900, ii, 606).—Desiccated yeast extract shows practically no falling off of fermentative activity after being kept for 12 months in a stoppered bottle (compare Abstr., 1900, ii, 236). The addition of 1 per cent. of sodium chloride or ammonium chloride to yeast extract only slightly diminishes its activity, but with 2 per cent. the effect is considerable; 1 per cent. of sodium, ammonium, or magnesium sulphate or 1 per cent. of sodium nitrate produces the same effect as 2 per cent. of sodium or magnesium chloride. The presence of 2 per cent. of calcium chloride totally prevents fermentation, although the same amount of barium chloride is almost without influence. Borax has a slightly less effect than common salt.

On adding salts of nitrous acid to fresh yeast extract, a considerable amount of nitrogen is evolved, probably owing to the decomposition of the tyrosine and leucine present (Geret and Hahn, Abstr., 1898, ii, 246).

When 100 grams of sucrose are fermented with yeast extract containing 2 per cent. of arsenious acid (as potassium arsenite), there are produced along with alcohol (50.4 grams) quantities of glycerol (0.5 gram) and succinic acid (0.3 gram) which are much smaller than those obtained by Pasteur in the case of yeast cells; the smallest amounts of glycerol and succinic acid hitherto observed to be formed with yeast cells range from 0.8—1.9 and 0.2—0.3 per cent. respectively of the weight of the sugar taken.

W. A. D.

Yeast Extract. By AUGUSTIN WRÓBLEWSKI (*Bull. Acad. Sci. Cracow*, 1901, 94—95. Compare Abstr., 1900, ii, 157).—The largest and most active portion of the yeast-extract is separated at a low pressure (about 46 kg. per sq. cm.) and is opalescent; further pressure separates a more transparent and less active liquid. The extract contains appreciable quantities of silicic acid, has no marked rotatory power, and can be filtered through a sandstone filter without losing its power of fermenting sugar. The filtrate from a fermenting sugar

solution was found to contain no zymase, but a small quantity of invertin, showing that the former acts only within the yeast-cell, but the latter partly outside it. The hydrolysis of sugar by invertin is a reversible change, and the enzyme has a slight synthetical action on invert-sugar. T. M. L.

Autofermentation of Yeast. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1901, 32, 59—78. Compare Salkowski, *ibid.*, 13, 506).—Fresh bottom yeast was thoroughly washed with ice-cold water, and then left in contact with toluene water at a temperature of 38° for some 14 days, when the liquid no longer gave the biuret reaction.

Among the products of fermentation isolated were hypoxanthine bases, leucine and tyrosine, together with ammonia, histidine, arginine, lysine, aspartic acid, and a compound, $C_8H_6O_4N_4$. The same products are formed when the liquid is kept faintly alkaline by the addition of sodium carbonate. Yeast thus contains an enzyme which in its method of fermentation resembles trypsin. Well nourished yeast does not undergo tryptic fermentation, and no hexon bases have been found in different beers.

J. J. S.

Action of Formaldehyde on Germination. By RICHARD WINDISCH (*Landw. Versuchs-Stat.*, 1901, 55, 241—252. Compare Abstr., 1898, ii, 40).—The experiments previously made with cereal seeds were repeated with a variety of leguminous and some other seeds. Solutions containing 0.02 per cent. of formaldehyde somewhat retarded the germination of linseed, but had no effect on lupins, peas, horse and soy beans; the germinating energy of lucerne and clover was somewhat diminished. The 0.05 per cent. solution greatly retarded the germination of clover and lucerne, and also had some retarding effect on lupins, peas, and beans. As regards the number of seeds which germinated, the 0.05 per cent. solution was found to be very injurious to peas, lucerne, clover, rape and flax, and injured lupins and beans. Solutions containing 0.2 per cent. of formaldehyde killed flax and rape, greatly injured lupins, peas, and clover, and retarded the germination of horse beans; maize was, however, not injured. A 0.4 per cent. solution killed almost all the seeds except maize.

N. H. J. M.

Presence of a Proteolytic Enzyme in Germinated Seeds. By WL. BUTKEWITSCH (*Zeit. physiol. Chem.*, 1901, 32, 1—53. Compare Abstr., 1900, ii, 744, and this vol., ii, 182).—The proteolytic enzyme of germinated *Lupinus* seeds is less active in 0.1 per cent. sodium hydroxide or in 0.2 per cent. hydrochloric acid; in the latter case, most of the products formed can be precipitated by phosphotungstic acid. The activity is increased by the addition of small amounts of hydrocyanic acid. J. J. S.

A Glucoside characterising the Germinating period of Beech. By P. TAILLEUR (*Compt. rend.*, 1901, 132, 1235—1237).—Beech seedlings contain a glucoside and a diastase which give rise to the production of methyl salicylate and dextrose. The glucoside does not exist in the seed or in old plants, and is produced during germination. It occurs mainly in the hypocotyledonary axes, and is not found in the

cotyledons or in the stems and leaves. (Compare Bourquelot, *J. Pharm.*, 1891; and Abstr., 1896, ii, 540.) N. H. J. M.

Composition of some Conifer Seeds. By ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1901, 55, 267—307. Compare Abstr., 1899, ii, 241 and 242).—The various seeds examined did not differ greatly in composition qualitatively. All of them contained invertible carbohydrates, including sucrose, probably, in every case. Four of the varieties of seeds contained carbohydrates which yielded mucic acid when oxidised. Starch occurred only in the seeds of *Pinus Cembra*. The seeds of *Abies pectinata* contained a volatile oil and a red dye.

The following percentage results were obtained with the various seeds. (1) *Picea excelsa*, (2) *Abies pectinata*, (3) *Larix europæa*, (4) *Pinus silvestris*, (5) *P. maritima*, and (6) *P. Cembra*.

| | Proteids. | Ether extract. | Lecithin. | N-free substances. | | Starch meal. | Crude fibre. | Ash. | P ₂ O ₅ . |
|----|-----------|-------------------|-----------|--------------------|-------|-----------------|-----------------|------|---------------------------------|
| | | | | (1). | (2). | | | | |
| 1. | 21·12 | 32·54 | 0·20 | 5·43 | 35·99 | — | 25·40 | 4·74 | — |
| 2. | 11·90 | 26·12 | 0·11 | 3·36 | 55·79 | — | 31·40 | 2·72 | 0·66 |
| 3. | 6·91 | 10·17 | 0·11 | 1·55 | 79·22 | — | 51·76 | 1·99 | — |
| 4. | 38·19 | 27·91 | 0·49 | 3·56 | 22·70 | — | 18·58 | 7·15 | 2·34 |
| 5. | 22·40 | 22·76 | 0·43 | 2·48 | 47·46 | — | 36·53 | 4·47 | 1·26 |
| 6. | 7·21 | 19·16 | 0·37 | 7·20 | 61·64 | 2·78 | 38·71 | 1·64 | — |

The two columns under nitrogen-free substances refer to the matter soluble in water (1), and that which is insoluble in water, malt-extract, and ether (2). The latter should always be determined in seeds in addition to crude fibre.

The results of analyses of the skins of seeds of *Pinus maritima* and *P. Cembra* are also given. N. H. J. M.

Occurrence of Zinc in the Vegetable Kingdom. By L. LABAND (*Zeit. Nahr.-Genussm.*, 1901, 4, 489—492).—The author has tested some plants grown in the neighbourhood of Scharley, in Upper Silesia, on soil containing zinc and situated close to the zinc mines.

One hundred grams of the well cleansed material dried at 100° were treated according to Halenke's directions with sulphuric acid and a little mercuric oxide; after boiling for about 8 hours, a colourless liquid was obtained. After diluting with water and filtering, the mercury was removed by means of hydrogen sulphide, and in the filtrate the zinc was estimated gravimetrically as zinc oxide, the result being 0·252 gram. In a duplicate experiment, the zinc was deposited by electrolysis, and 0·2018 gram of metallic zinc was obtained.

Reference is made to the work of a large number of investigators who have examined plants grown on soil containing natural or added zinc compounds. L. DE K.

Formation of Asparagine in Plants. By ERNST SCHULZE (*Chem. Centr.*, 1901, i, 1108—1109; from *Landw. Jahrb.*, 30, 287—297. Compare Abstr., 1898, ii, 481; 1900, ii, 612, 745).—The decomposition of proteids in seedlings is due to a hydrolytic action, identical with that brought about by acids or trypsin. The asparagine formed is mainly derived from secondary reactions taking place

between amino-acids and other decomposition products of proteids, but a small quantity may possibly be formed by direct decomposition.

E. W. W.

Beans as Food Material in Servia. By ALEXANDER ZEGA and DOBR. KNEZ-MILOJKOVIĆ (*Chem. Zeit.*, 1901, 25, 396—397).—The authors have analysed a number of different kinds of beans, which are largely made use of by the Servians, both in the raw, green state, and also in the ripe and cooked condition.

J. J. S.

Nori from Japan. By KINTARO OSHIMA and BERNHARD TOLLENS (*Ber.*, 1901, 34, 1422—1424).—Nori is a human food material prepared in Japan from sea algæ (*Porphyra laciniata*) and consists of thin, greenish, paper-like leaves insoluble in water and almost tasteless.

When distilled with hydrochloric acid, nori yields both furfuraldehyde and methylfurfuraldehyde. Oxidation with nitric acid gives mucic acid to the amount of 6.73 per cent. of the weight of nori, besides saccharic acid. The liquid obtained by extracting the substance with dilute hydrochloric acid at 70° gives a beautiful red colour with resorcinol, the presence of fructose or other ketoses being thus indicated.

When hydrolysed with dilute sulphuric acid, nori yields *i*-galactose, *d*-mannose, and probably a small quantity of fucose.

T. H. P.

Manurial Experiments. By JOHN SEBELIEN (*Bied. Centr.*, 1901, 30, 301—305; from *Tidskr. Norsk. Landbr.*, 1901, 8, 69—78).—The results of pot experiments in which oats and peas were grown in peaty soil manured with finely powdered apatite and basic slag respectively, in addition to lime and potassium chloride, accorded with those obtained by Nilson and von Feilitzen, showing that apatite, even finely powdered, has very little effect.

Felspar, as compared with soluble potassium salts, was shown to be of very little use.

Experiments with oats grown in sandy soil, manured with potassium sulphate, calcium carbonate, sodium nitrate, and with various phosphates in addition, gave the following amounts of total produce, taking the produce of a pot which had no phosphates as 100: basic slag (3.9 grams), 931; Peru guano (1, 4.35 and 2, 2.90 grams), 709 and 737; fish guano (3.95 grams), 738; whale guano (6.80 grams), 170; and bone meal (2.10 grams), 706. The varying results which have been at different times obtained with bone meal are attributed to differences in the soil bacteria.

Covering the soil (peat) with sand (15 cm.) considerably increased the yield of peas, but did not give satisfactory results with oats. Application of nitrogen to peas growing in peat-soil greatly increased the produce.

N. H. J. M.

Sugar Beet in Alkali Soil. By H. C. MYERS (*J. Soc. Chem. Ind.*, 1901, 20, 445—448).—The samples of sugar beet examined were grown on the alkali soil of Hooper, Utah, near the Great Salt Lake. Analyses of the soils are also given. The results, showing the percentage of sugar in the beet, and the purity coefficients, indicate that the crop is especially suitable for soils containing amounts of

alkali which prohibit the growth of other crops. The tendency of beet is to improve such land for other crops by taking up the excess of alkali.

As regards the relation between the shape and condition of the roots and the percentage of sugar and the purity, a number of analyses are given of selected roots. It was found that small roots contain the highest percentage of sugar, and that long roots show the highest purity coefficients. Small, slender roots obtained by deep tillage and a limited supply of water are the best.

N. H. J. M.

Fish Meal and its Future in Germany. By FRANZ LEHMANN (*Bied. Centr.*, 1901, 30, 334—337; from *Hannov. Land. Forstwirtschaft. Zeit.*, 1900, 193).—Three samples of Norwegian fish guano contained: proteids, 49.7—54.8; fat, 0.93—1.58; ash, 34.24—37.56, and water, 10.4—12.1 per cent. Whale meal was found to contain: proteids, 67.52; fat, 8.10; ash, 2.93, and water, 9.67 per cent. Feeding experiments were made in which cows received 1.5 kilo. of whale meal; this amount had no injurious effect on the taste of the butter.

Herring cake is made by compressing a mixture of crushed grain and herrings; the cake is then dried. The results of feeding experiments by Hennings showed that the taste of butter was not affected at first; subsequently, however, the butter acquired a fishy taste. Herring meal was without influence on milk, cream, and butter.

In some parts of Germany, fish, both raw and cooked, is used for feeding pigs; the meat has an oily taste, and the fat is soft and is yellow or greyish. The effect on the meat of feeding with fish is, however, overcome by feeding for four to six weeks with grain. A more suitable food, a fish meal containing very little fat, is prepared from sticklebacks. Cows received 1 kilo. of the meal without injury to the milk, whilst sheep and pigs had 300 grams per day up to the time they were killed without the quality of the meat being affected. The composition of the meal was as follows: proteids, 62.2; fat, 1.5; water, 11.7; ash, 22.5 (containing $P_2O_5 = 9.5$ per cent.).

N. H. J. M.

Feeding Experiments with Molasses and Peat Meal. By OSCAR KELLNER, O. ZAHN, and H. VON GILLERN (*Landw. Versuchs-Stat.*, 1901, 55, 379—388).—The results of experiments with sheep showed that peat meal is quite indigestible, and that it causes the passage into the faeces of substances which would otherwise be retained or utilised in other ways. The beneficial effect of peat molasses in diminishing colic is due to the molasses and not to the peat.

N. H. J. M.

Feeding Experiments on Cows with Palm Kernel Cake, Crushed Palm Kernels, and Linseed, Ricinus, and Earth Nut Meals. By EBERHARD RAMM, C. MOMSEN, and TH. SCHUMACHER (*Bied. Centr.*, 1901, 30, 321—322; from *Milch-Zeit.*, 1900, Nos. 19, 20, 22 and 23).—Linseed meal gave the highest yield of milk fat; the butter fat had the highest iodine number, which accords with the observation frequently made that linseed meal produces soft-butter.

With palm kernel cake, less milk was produced, but nearly as much butter fat, the percentage of fat in the milk being much the highest; the butter was hard, the butter fat not containing much olein. Palm kernels (crushed) were not quite equal to the cake, but form a convenient food.

Earth nut meal is not recommended. Ricinus meal gave the worst results, but it is not injurious. N. H. J. M.

Cause and importance of Decomposition of Nitrates in Soil. By W. KRÜGER and W. SCHNEIDEWIND (*Bied. Centr.*, 1901, 30, 314—317; from *Landw. Jahrb.*, 1900, 29, 747. Compare Abstr., 1899, ii, 510).—In accordance with previous results, it was found that pentosans from straw caused the greatest destruction of nitrates. Cotton wool caused denitrification, but not to the same extent as crude fibre from straw. Cellulose does not seem to be directly available as food for denitrifying bacteria, but must be first decomposed by other organisms. Peat had no effect, and pentosans extracted from peat only a slight effect. Both sucrose and starch caused considerable reductions in the yield of mustard, this being due to denitrification.

Experiments were made with stable manure which had been kept a year and had lost 41.9 per cent. of dry matter, but no nitrogen, and with similar manure, kept fresh by sterilising, showed that the fresh manure was very injurious, whilst the decomposed manure was decidedly beneficial.

The results of field experiments, in which cow dung, wheat straw, and horse dung were applied, showed in each case diminished yields.

N. H. J. M.

Phosphoric Acid in Soils. By TH. SCHLÖSING, jun. (*Compt. rend.*, 1901, 132, 1189—1191. Compare Abstr., 1899, ii, 119 and 243).—Determinations of phosphoric acid soluble in water were made by agitating the soil (300 grams) with water (1300 c.c.); 1000 c.c. of the solution were then decanted and the same amount of water added to the 300 c.c. remaining with the soil. The process was repeated as long as phosphoric acid continued to be dissolved. Results obtained with three different soils showed that they contained respectively 440, 210, and 130 kilograms of soluble phosphoric acid per hectare.

The results of experiments made by the author (*loc. cit.*) and by Artus (*Ann. Sci. agron. franç. étrang.*, 1901) indicate that the phosphates dissolved in soil water are utilised by plants. Artus's results obtained with light soils showed that the amounts of phosphoric acid soluble in water which they contained corresponded with their wheat producing power.

The extraction of soils with very dilute nitric acid (1—2:10000) (Abstr., 1899, ii, 449) gave results indicating that the phosphoric acid dissolved follows, in the different soils, the amounts dissolved by water. Similar experiments with Hungarian soils have been made by A. de Sigmond (*Ann. Sci. agron. franç. étrang.*, 1900), who considers that 0.075 per cent. of phosphoric acid, soluble in the dilute acid (1000 c.c. of acid to 25 grams of soil), is the limit beyond which an application of phosphatic manures is unnecessary.

N. H. J. M.

Condition of Aluminium in Vegetable Soils. By THÉOPHILE SCHLÖESING (*Compt. rend.*, 1901, 132, 1203—1212).—The results of experiments with a number of Madagascar soils show that most of them contain either free alumina or aluminium silicates readily attacked by dilute sodium hydroxide solution. The alumina and the silica are chiefly in a sandy condition and do not add to the tenacity of the soils.
N. H. J. M.

Action of the Phosphoric Acid and the Nitrogen in "Leipzig Poudrette" and in "von Krottnaurer's Patent Manure." By O. BÖTTCHER (*Bied. Centr.*, 1901, 30, 310—313; from *Sächs. landw. Zeit.*, 1900, No. 38).—Leipzig poudrette contains N, 4—5; K_2O , 4—5; and P_2O_5 , 4—5 per cent. Von Krottnaurer's patent manure is prepared from slaughterhouse refuse, &c., by treating with sulphuric acid; one kind contains N, 6, and P_2O_5 , 6 per cent.; the other N, 5, and P_2O_5 , 9 per cent. Pot experiments with oats were made in which the manurial effect of the manures was compared with that of double superphosphate and sodium nitrate. The following values were obtained, taking those of the superphosphate and of the nitrate as 100. Effect as phosphatic manure, (1) Leipzig poudrette = 89·8; (2) von Krottnaurer's manure = 94·6. Effect as nitrogenous manure, (1) 43·3; (2) 43·3.
N. H. J. M.

Basic Superphosphate, its preparation and use as a Manure. By JOHN HUGHES (*J. Soc. Chem. Ind.*, 1901, 20, 325—328).—The manure is prepared by mixing superphosphate (85 parts) with slaked lime (15 parts) and allowing the mixture to remain in a heap for 24 hours. Superphosphate, containing soluble phosphate 27·72, and insoluble phosphate 4·82 per cent., treated in this manner, yielded basic superphosphate containing 26·19 per cent. of phosphate soluble in 0·1 per cent. citric acid (1000 c.c. to 1 gram of manure). Of the total substance, 94·7 per cent., containing CaO, 34·66, and P_2O_5 , 12·00 per cent., dissolved in the dilute acid. Cold water dissolved 66·8 per cent., containing CaO, 33·20 per cent., but no phosphoric acid; whilst 2·5 per cent. ammonium citrate solution (100 c.c. to 1 gram of substance) dissolved 86·70 per cent., containing CaO, 32·03, and P_2O_5 , 10·20 per cent.
N. H. J. M.

Analytical Chemistry.

Some Blowpipe Tests. By JOSEPH W. RICHARDS (*J. Amer. Chem. Soc.*, 1901, 23, 213—215).—*Closed Tube Test* —Water, volatile sulphur, &c., may be estimated with considerable accuracy by heating the substance in a closed tube. The part of the tube containing the sublimate is nicked with a file, broken off, and weighed; the sublimate or condensed water is then driven off by heating, and the tube reweighed.

Open Tube Test.—The test is uniformly trustworthy if the mineral is finely powdered and finally heated as strongly as possible without melting the glass. When testing the minerals alledmontite, dyscrasite and ullmannite, only antimonious oxide is obtained and when the upper part of the tube from which the vapours are escaping is held in the flame, this is coloured pale yellowish-green; in the case of arsenic the coloration is pale blue.

Flame Tests.—When testing for phosphoric acid, the assay on platinum wire is touched when hot with sulphuric acid and brought into the outside edge of the Bunsen flame as low down as possible. The flame will be slightly bluish-green close to the wire, green a short distance away, and yellowish-green farther off. When testing for boron, the wire should be held an inch higher in a hotter part of the flame; when using Turner's mixture, it is best to moisten with sulphuric acid and then place in the edge of the flame.

Reduction to Metal.—In some cases, notably of tin oxide, borax is often preferable to potassium cyanide when reducing with sodium carbonate on charcoal.

Test for Fluorine.—The substance is fused with potassium hydrogen sulphate in a large closed tube of 5 to 8 mm. diameter, heating regularly with the tube almost horizontal. The silica ring deposits just above the assay, and the odour of the gas is often quite perceptible. The tube when cold is broken below the silica ring, and the upper end is held vertically close to the nose when the odour of hydrogen fluoride may be detected with certainty; moreover, the ring will be found to be insoluble in water.

Test for Arsenates.—The substance is mixed with sodium carbonate and charcoal dust, and put into the lower end of an open tube; by playing on it with the reducing flame of the blowpipe directed into the tube, an arsenical coating will be obtained. The test also answers for mercury compounds, antimonates, tellurates, and selenates, whilst ammonium compounds yield ammonia.

Test for Silica in the Sodium Metaphosphate Bead.—It is stated that when testing for silica with microcosmic salt, the silica skeleton is not always left undissolved and sometimes may disappear altogether, as in the case of thaumasite and other minerals; free silica is, however, but very slightly dissolved. As, however, the solution of the silica always takes place slowly and with difficulty and causes a milky opalescence, with a little practice its detection is comparatively easy.

L. DE K.

Estimation of dissolved Oxygen in Waters in presence of Nitrites and of Organic Matter. By SAMUEL RIDEAL and C. G. STEWART (*Analyst*, 1901, 26, 141—147).—The authors use Winkler's manganous chloride process, but, beforehand, oxidise the organic matters and the nitrites. After ascertaining by a preliminary experiment how much *N/10* permanganate is necessary to communicate a pink colour, lasting for 10 minutes, to the acidified water, they operate as follows: 1 c.c. (or 2 c.c. if more than 10 c.c. of permanganate are used) of sulphuric acid is placed in a Winkler's bottle, the requisite amount of *N/10* permanganate is introduced, the bottle is filled with

the sample taken straight from the source, closed, and left for ten minutes. The bottle is momentarily opened and 0.5 c.c. of a 2 per cent. solution of potassium oxalate is added to reduce the excess of permanganate.

One c.c. of a 33 per cent. solution of manganous chloride is now passed to the bottom of the bottle from a long pipette, followed by 3 c.c. of a solution containing 50 per cent. of sodium hydroxide and 10 per cent. of potassium iodide. The stopper is inserted and the contents mixed by inversion and rotation. When the liquid has become clear, the stopper is quickly removed, 3 c.c. of hydrochloric acid are introduced, the stopper is re-inserted, and the bottle well rotated for 5 minutes in a dark place. The liberated iodine which represents the free oxygen is then titrated as usual. The correction for the volume occupied by the reagents is small and may usually be neglected. When, however, the amount of oxygen is low, the reagents being presumably saturated with oxygen under atmospheric conditions will make the result too high. The correction then to be applied is: $x = (1000a - Rn)/V - n$, in which x is the number of c.c. of oxygen per litre of the liquid, a the amount of oxygen in c.c. found by titration, V the volume of the bottle, and n that of the reagents, whilst R is the number of c.c. of oxygen contained in a litre of saturated water at the temperature of the experiment which may be actually estimated, or obtained by reference to Roscoe and Lunt's table (Trans., 1889, 55, 532).

L. DE K.

Estimation of Water in Mixtures of Organic Substances and Sodium Hydrogen Carbonates. By JOSEF KÖNIG (*Zeit. Nahr. Genussm.*, 1901, 4, 448—449).—The water is estimated by heating the substance in a glass tube placed in an air-bath at 100—105° while transmitting a current of dry air. The water vapour is absorbed in a weighed calcium chloride tube.

L. DE K.

[**Estimation of Sulphur in Commercial Benzene intended for enriching Illuminating Gas.**] By WILFRID IRWIN (*J. Soc. Chem. Ind.*, 1901, 20, 440—442).—The ordinary Letheby apparatus for the estimation of the total sulphur in coal gas is employed, the gas burner being replaced by a spirit lamp in which are placed 10 c.c. of the benzene and 90 c.c. of alcohol or methylated spirit, and the flame is surrounded with pieces of ammonium sesquicarbonate in the usual manner. The results obtained are considerably higher than those yielded by the method of Holland and Philips (*J. Soc. Chem. Ind.*, 1884, 296).

M. J. S.

Analysis of Strong and Fuming Sulphuric Acid. By H. RABE (*Chem. Zeit.*, 1901, 25, 345—346).—An acid containing exactly 95 per cent. of H_2SO_4 is added from a burette to 25 c.c. of fuming sulphuric acid until fumes are no longer evolved when air is blown through the liquid; say 24.8 c.c. are required. The experiment is now repeated with the sample to be tested when, say, 30.5 c.c. are required. The percentage of water in the sample will then be found by multiplying 24.8 by 5, and dividing by 30.5.

The amount of free sulphur trioxide in fuming acid may be

estimated by taking 25 c.c. of the sample and adding 95 per cent. acid until fumes are no longer evolved; the experiment is then repeated, using a fuming acid containing a known weight of sulphur trioxide, say, 30 per cent. If the standard acid requires 59.4 c.c., and the sample 49.8 c.c. of 95 per cent. acid, the amount of free sulphur trioxide in the latter will be found by multiplying 49.8 by 30 and dividing by 59.4.

L. DE K.

Standardisation of Thiosulphate Solution. By PERRIN (*Chem. Centr.*, 1901, i, 1115; from *Mon. Sci.*, [iv], 15, i, 244).—Iodine is liberated from a mixture of potassium iodide and iodate by the action of a known quantity of normal sulphuric acid, and is used for standardising the thiosulphate. Both the iodide and thiosulphate employed must be absolutely neutral.

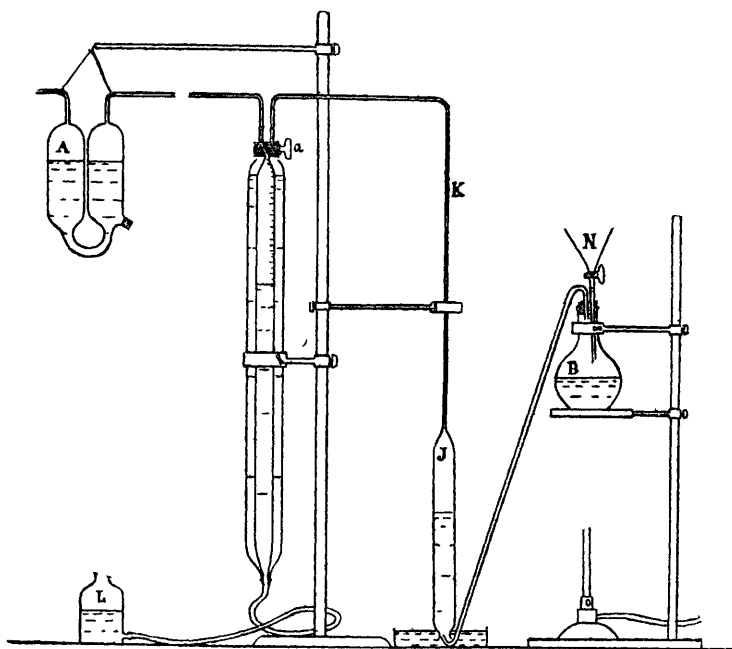
M. J. S.

[Estimations with the] Nitrometer. By C. H. SHEPARD (*J. Amer. Chem. Soc.*, 1901, 23, 267—268).—The author has treated 0.5 gram of potassium nitrate with 32 c.c. of sulphuric acid of varying strength in the nitrometer at 20°. The strongest (98.03 per cent.) acid yielded 222 c.c. of nitric oxide calculated on 1 gram of nitre, whilst the weakest (80.14 per cent.) acid yielded 226.2 c.c. If this difference of 4.02 c.c. (or 2.01 c.c. per 0.5 gram) is due to the difference in solubility of nitric oxide in these two acids, then 32 c.c. of the strong acid absorbs 2.01 c.c. of nitric oxide or 0.0628 c.c. per c.c.; this does not agree with a statement by Lunge (*Abstr.*, 1885, 954) according to which the solubility amounts to only 0.035 c.c. When using the nitrometer, the author prefers an acid of 95 per cent. strength.

L. DE K.

Apparatus for the Estimation of Nitrogen in Nitrates by the Schulze-Tiemann Method. By VL. STANĚK (*Zeit. Zuckerind. Böhm.*, 1901, 25, 356—358).—In the estimation of nitrogen by this method, the nitrate is boiled with a hydrochloric acid solution of ferrous chloride, the nitric oxide evolved being collected in a graduated tube over dilute alkali solution; the tube is then transferred to a tall cylinder filled with recently boiled water, and after a time the volume and temperature of the gas are read off. In order to avoid this transference of the measuring tube, the author has devised the apparatus shown in the figure. It consists of a flask, *B*, which is fitted with a tap funnel, *N*, and a gas delivery tube, and contains the ferrous chloride solution and the hydrochloric acid. This mixture is boiled until the flask is completely air-free. While this is going on, the two-way cock, *a*, is so adjusted that the capillary tube, *K*, is connected with the burette, the bottle, *L*, containing water being then manipulated so that the vessel, *J*, and the capillary, *K*, become filled with dilute alkali solution. The cock, *a*, is next turned through 180°, the air expelled from the burette by raising the bottle, *L*, and the cock closed, the apparatus then being ready for use. When *B* is quite air-free, the end of the delivery tube is placed beneath the mouth of *J*, which dips below the surface of a basin containing dilute alkali solution. A measured volume of previously boiled nitrate solution is now introduced into the flask, *B*, by means of the funnel, which is washed with boiled water, the boiling of the liquid being then continued so long as gas bubbles

are evolved. When all the gas has been given off, it is drawn over into the burette, care being taken that the hot liquid does not enter the burette. After a few minutes, the levels of the liquid in the bottle, *L*, and in the burette are equalised, and the volume and temperature of the gas read off. To test the purity of the nitric oxide collected, it is



driven from the burette into the absorption vessel, *A*, containing either saturated ferrous sulphate solution or alkaline potassium permanganate solution; should there be any unabsorbed residue, it is returned to the burette and its volume subtracted from that of the total quantity of gas.

T. H. P.

Estimation of Nitro-groups by a Volumetric Method. By PAUL ALTMANN (*J. pr. Chem.*, 1901, [ii], 63, 370—380).—A weighed quantity of the nitro-compound is added to a known volume of a standard solution of stannous chloride. After warming the mixture for a short time, it is made up to a given volume, of which an aliquot part is taken and added to excess of an alkaline solution of Rochelle salt. The remaining stannous chloride is now titrated with *N*/10 iodine solution, or with potassium permanganate. The details of preparation of the solutions are given in the paper. Standard iodine is inapplicable when much colour is developed, as with mono- or di-nitrophenols, in which case permanganate is used. The method cannot be employed for trinitrophenol or nitronaphthalene.

K. J. P. O.

Rapid Estimation of Phosphoric Acid Soluble in Water in Superphosphates. By LADISLAUS VON SZÉLL (*Landw. Versuchs-Stat.*, 1901, 55, 325—346).—Variations in the results of determinations of soluble phosphoric acid are due to the want of uniformity in the samples of superphosphate; to the extraction being more or less incomplete; to insufficient filtration, and to the use of different methods in determining the phosphoric acid. The following method is proposed.

The sample is rubbed through a 3 mm. sieve and mixed. Twenty grams are then well mixed with water in a mortar, slowly diluted with water, and decanted into a litre shaking-flask. This is repeated four or five times, the residue being finally washed into the flask, which is then nearly filled with water. The flask is then agitated for 15—30 minutes, filled to the mark, and filtered. A portion of the filtrate (50 c.c.) is treated first with sufficient citrate solution (citric acid, 300 grams and 1 litre of 24 per cent. ammonia diluted to 3 litres with water), being stirred all the time, to dissolve the precipitate first produced; and then with one-tenth of this amount of the same solution. Magnesia mixture (25 c.c. is usually sufficient) is then added. After 6—12 hours, it is filtered, washed with 2·5 per cent. ammonia, and dried at 100—120°. The filter containing the precipitate is slowly burnt in a platinum crucible and afterwards heated until white.

N. H. J. M.

Arsenic in Coal and Coke. By R. F. WOOD SMITH and ROBERT LEONARD JENKS (*J. Soc. Chem. Ind.*, 1901, 20, 437).—The contamination of malt with arsenic from the use of an arsenical fuel in the kiln drying is mainly dependent on the proportion of that element which volatilises during the combustion. The following method has therefore been employed to estimate the "volatile" and "fixed" arsenic respectively. A piece of combustion tube about 20 inches long is drawn out at one end to a neck 2—3 mm. in diameter, which is bent at a right angle and passed through the rubber stopper of a wash-bottle containing dilute sulphuric acid. About an inch from this neck the tube is constricted at a second place so as to leave a bulb, and then 6—8 inches of the tube are filled with the fuel in fragments about the size of a pea. The fuel is burnt by heating the tube whilst aspirating air in the direction of the wash-bottle, care being taken that the products of combustion do not pass over the ash. The tube is then severed at the constriction, the bulb is washed into the acid, and the volatile arsenic estimated by the Marsh apparatus. The ash of the fuel may also be dissolved in dilute sulphuric acid for the estimation of the fixed arsenic. The numbers so obtained agreed well with those of practical work.

M. J. S.

Determination of Minute Quantities of Arsenic in Coke. By LEONARD ARCHBUTT and PERCY GEORGE JACKSON (*J. Soc. Chem. Ind.*, 1901, 20, 448—450).—The powdered coke (50 grams) is gently boiled for 2 hours with 100 c.c. of nitric acid of sp. gr. 1·42 in a retort with the neck inclined upwards, which answers the purpose of a reflux condenser. The solution is diluted, filtered, and repeatedly evaporated, after adding sulphuric acid, until every trace of nitric acid is expelled. It is then distilled with addition of 23 grams of pure

sodium chloride and 2 grams of ferrous sulphate, the total volume not exceeding 100 c.c. When the temperature reaches 125°, all the arsenic will have distilled over. It is collected in about 20 c.c. of water, and precipitated by adding zinc sulphide to the acid distillate. The precipitate is collected, washed, and then dissolved by boiling it with 300 c.c. of water for half an hour. The solution is concentrated to 40 c.c., mixed with sodium hydrogen carbonate and starch, and titrated with *N*/100 iodine. Blank experiments with the reagents used are necessary, and the iodine solution must be standardised with arsenious sulphide dissolved in the same manner.

M. J. S.

Special Crucible for Carbon Combustions. By PORTER W. SHIMER (*J. Amer. Chem. Soc.*, 1901, 23, 227—228).—The author has modified his arrangement for the combustion of free carbon in a platinum crucible (*Abstr.*, 1899, ii, 694), and instead of cooling the upper part by means of a wet wick the crucible is now fitted with an annular platinum cooling chamber about 1/2 inch wide and 1/8 inch deep, having short platinum inlet and outlet tubes at opposite sides. The water after flowing through the stopper is conducted to the cooling chamber of the crucible by bent glass and rubber tubing, through which it flows to waste.

The rubber band by which the crucible is tightly closed is effectually cooled on its inner side by contact with the cold stopper, and on its outer side by contact with the cold top of the crucible. Two drawings are given showing the exact position of the tubes for the inlet and outlet of the air or oxygen. If the apparatus is used for determining combined water in minerals, cements, &c., the circulating water should be heated to prevent condensation of water-vapour on the stopper.

L. DE K.

A Rapid Method of Estimating Carbon Dioxide in Air. By JOHN S. HALDANE (*J. Hyg.*, 1901, 1, 109—114).—A portable piece of apparatus is described and figured by means of which the amount of carbon dioxide in air can be determined by absorption in potassium hydroxide, within five minutes, and without any calculations.

W. D. H.

Estimation of Calcium, Magnesium, and Phosphoric Acid in the Presence of a notable proportion of Iron Oxide. By HENRI PELLET (*Ann. Chim. anal. appl.*, 1901, 6, 163—165).—The author states that when estimating calcium in acetic acid solution by means of ammonium oxalate without removing any large excess of iron which it may contain, it is necessary to add 15 or 20 times more of the reagent than is required in the absence of iron. To estimate magnesium in the presence of calcium and much iron, a much larger excess of ammonium citrate than usual should be added, followed by a large excess of sodium phosphate and ammonia. For the estimation of phosphoric acid, the liquid is mixed with about 20 drops of solution of ammonium citrate to prevent precipitation of free molybdic acid and then treated as usual with molybdate solution. The yellow precipitate is purified by dissolving it in ammonia and reprecipitating

with dilute nitric acid ; it then, after drying at 100° , contains exactly 3.75 per cent. of phosphoric oxide.

L. DE K.

Estimation of Metals by Organic Bases. By W. HERZ (*Zeit. anorg. Chem.*, 1901, 27, 310—311).—The method previously described by the author (this vol., ii, 240, 348) gives accurate results with the following metals. Copper is completely precipitated by guanidine, and a cold solution of piperidine precipitates salts of copper, magnesium, and zinc.

Tetramethylammonium hydroxide also gives quantitative precipitates with metallic salts, but this precipitate is so gelatinous that it is exceedingly difficult to wash.

E. C. R.

Electrolytic Separation of Lead from Manganese. By IVAR MOLTKE-HANSEN (*Chem. Zeit.*, 1901, 25, 393—395).—Lead may be precipitated by electrolysis as dioxide free from manganese by operating as follows. If the solution which should contain about 0.2 gram of lead in 150 c.c. contains also an amount of manganese not exceeding 0.03 gram, the liquid should contain 25—27 c.c. of nitric acid of sp. gr. 1.42 or 55—60 c.c. of acid of sp. gr. 1.19, and should be electrolysed at 70° with a current of 2 amperes. The lead is completely precipitated in 35—40 minutes.

If the amount of manganese reaches 0.04 gram, fairly accurate results may still be obtained by adding 35 c.c. of nitric acid of sp. gr. 1.42 and using a current of $2\frac{1}{2}$ amperes, or, better still, by adding the same amount of nitric acid as before, and afterwards a little oxalic acid to redissolve any precipitate of manganese dioxide ; a few more c.c. of nitric acid may then also be added.

L. DE K.

Cyanogen Compounds of Silver and Copper in Gravimetric Analysis. By OTTO BRUNCK (*Ber.*, 1901, 34, 1604—1609).—Cold dilute nitric acid has no action on even freshly precipitated silver cyanide, but on warming with 1 per cent. acid for an hour, 5 per cent. of the salt dissolves, and only part is reprecipitated on cooling. The amount dissolved is somewhat less if an excess of hydrocyanic acid is present. Treatment with warm dilute nitric acid is not an accurate method for the separation of silver and copper cyanides, as an acid sufficiently strong (5 per cent.) to dissolve the copper cyanide has an appreciable solvent action on the silver compound. In the absence of copper, however, the method may be employed for the estimation of silver provided the acid is sufficiently dilute and the precipitation is carried out below 50° .

Silver and copper may be separated electrolytically provided sufficient potassium cyanide is present to render the ionisation of the complex copper salt practically *nil*. With 2 grams of potassium cyanide in 100 c.c. of liquid, a current of 4 volts and 0.5 ampere may be employed. If paracyanogen separates during the electrolysis, it is advisable to add a little potassium hydroxide. The current must be maintained while the deposit is being washed.

J. J. S.

Analysis of Commercial Copper. By AUGUSTE HOLLARD (*Ann. Chim. anal. appl.*, 1901, 6, 162—163. Compare Abstr., 1900, ii, 442).—Truchot having stated that the author does not include manganese among

the impurities of commercial copper, although it is found in notable quantities in Boleo and Arizona copper, the author has tested two samples of supposed manganiferous copper from Boleo, sent at his request by Truchot. After carefully removing any accompanying dross, which no doubt was very rich in manganese, the metal was carefully tested and found to be perfectly free from that impurity.

L. DE K.

Action of Potassium and Sodium Hydroxides on Stannous Sulphide. By F. MOLLWO PERKIN (*J. Soc. Chem. Ind.*, 1901, 20, 425—426).—The behaviour of precipitated stannous sulphide with solutions of the alkali hydroxides is not uniform. Even when the conditions of precipitation are seemingly identical, the precipitate sometimes dissolves, but more often does not. In cases where solution took place, a subsequent precipitation of metallic tin frequently occurred. The alkali hydroxides should therefore never be employed for the separation of the sulphides of the arsenic group from those of the copper group when the presence of stannous sulphide is possible. Stannic sulphide, and the sulphides of arsenic and antimony dissolve readily, but are incompletely precipitated on acidifying, unless hydrogen sulphide is added.

M. J. S.

Iodometric Estimation of Antimonic Acid and the Volumetric Estimation of Antimony in presence of Tin. By MARTIN ROHMER (*Ber.*, 1901, 34, 1565—1568).—Antimonic acid, like arsenic acid, is rapidly reduced by sulphur dioxide in presence of hydrochloric acid and traces of hydrobromic acid (this vol., ii, 194), and can be estimated, after boiling to remove sulphur dioxide, by adding tartaric acid, neutralising with sodium nitrogen carbonate, adding an excess of about 1 c.c. of an *N*/20 solution of iodine, and titrating back with sodium thiosulphate, using starch as an indicator; this method gives far better results than that of Mohr.

In presence of tin, the oxidation by iodine of antimony trioxide to antimonic acid is greatly retarded, but this difficulty can be obviated by using large quantities (10—20 grams) of tartaric acid. The mixed sulphides of tin and antimony are dissolved in concentrated hydrochloric acid containing potassium chlorate in an inclined flask of 300—500 c.c. capacity; after boiling to remove chlorine, 1 gram of potassium bromide is added, the solution boiled with aqueous sulphur dioxide, and then titrated with iodine as just described. When arsenic is present, it is removed in the beginning by distillation (*loc. cit.*).

W. A. D.

Estimation of Dry Matter in Soils. By H. PUCHNER (*Landw. Versuchs-Stat.*, 1901, 55, 309—324. Compare *Abstr.*, 1895, ii, 544).—A reply to Tryller (*Abstr.*, 1897, ii, 523). After drying the sample at 105° in a Soxhlet or Ulsch drying apparatus, the vessels containing the dry soil should be closed before being put into a desiccator to cool, and only opened for a moment before weighing. The substance should be well ventilated during drying, so as to avoid any accumulation of gases from the burner. The drying oven is to be heated to 105° before putting the substance in, and the temperature should be kept as uniform as possible.

N. H. J. M.

Chemico-toxicological Detection of Bromoform and Bromal. By DIOSCORIDE VITALI (*Chem. Centr.*, 1901, i, 1067; from *Boll. Chim. Farm.*, 40, 173—178).—Hydrogen which has been passed through a liquid containing bromoform, and is then ignited on the surface of brass wire gauze, burns with a characteristic blue flame. If the products of combustion are passed through ammonia, the ammonia becomes blue, and bromine can be detected in it by silver nitrate, or by evaporating and examining with the microscope for crystals of ammonium bromide. If the hydrogen containing bromoform vapour is passed over solid potassium hydroxide moistened with thymol, the latter becomes violet; if passed through alcoholic potash to which a little aniline has been added, the characteristic odour of phenylcarbamine is developed. Or the hydrogen may be passed through alcoholic potash and the liquid be boiled and evaporated to dryness; on adding concentrated sulphuric acid and cupric sulphate, blackish-violet cupric bromide is produced. Or the residue may be neutralised with acetic acid, treated with uric acid and some potassium bromate, and evaporated to dryness; then, on adding ammonia, the murexide reaction is obtained. For quantitative estimation, the liquid may be cohobated with alcoholic potash, and the resulting potassium bromide determined.
M. J. S.

Detection of Methyl Alcohol in Vinegar. By R. ROBINE (*Ann. Chim. anal. appl.*, 1901, 6, 171—174; continued from this vol., ii, 353).—In order to get trustworthy results, the dimethylaniline should be tested as to its purity. One c.c. is heated in a corked flask with 50 c.c. of water and 2—3 drops of acetic acid for $2\frac{1}{2}$ hours at 70—80°, the excess of dimethylaniline is then boiled off, and the colour test is applied; if this gives a negative result, the product may be used, but otherwise it should be purified by fractional distillation. It is also very important to expel all traces of acetaldehyde, although if the distillation is carried further than necessary there is great risk of losing methyl compounds. The sodium hydroxide should not be added in a too large excess and the excess of dimethylaniline should be completely boiled off. The purity of the lead dioxide used in the final colour reaction is also of great importance; it should be well washed with water to remove possible traces of alkali hypochlorites. In applying the dioxide, it should be added in small portions to the boiling liquid as a large excess destroys the blue colour. With these precautions, it is possible to demonstrate the presence of 0.1 per cent. of methyl alcohol.
L. DE K.

Estimation of Soluble Nitrocellulose in Gun-cotton and Smokeless Powder. By K. B. QUINAN (*J. Amer. Chem. Soc.*, 1901, 23, 258—264).—The proportion of soluble matter is best estimated by determining the amount of insoluble matter as follows.

One gram of the finely divided dry sample of gun-cotton or smokeless powder is introduced into an aluminium vessel and well stirred with 50 c.c. of alcohol, 100 c.c. of ether are then added and the whole again well stirred for several minutes. After removing the rod, the vessel is placed in one of the cups of a centrifugal machine and covered with a loosely fitting aluminium cap. In the second cup is placed

another aluminium vessel similarly filled. The machine is now started gradually and then run at full speed for 10—12 minutes. This causes the insoluble matters to collect at the bottom of the vessel, and the supernatant liquid may then be drawn off with a vacuum pipette. The residue is now freed from soluble matter by repeatedly whirling with successive quantities of ether-alcohol mixture, and then transferred to a Gooch crucible provided with the usual pad of asbestos; it is then dried at 100° and weighed.

In some cases, acetone may be substituted for ether-alcohol.

L. DE K.

Some Analyses of Pure Oatmeal. By BERNARD DYER (*Analyst*, 1901, 26, 153—154).—A table is given showing the result of the analysis of 13 samples of fine oatmeal, 6 samples of coarse oatmeal, and 8 samples of crushed or flattened oats. The figures given are those relating to moisture, oil, nitrogen, proteids ($N \times 6.25$), total ash and portion soluble in hydrochloric acid, the indigestible fibre and starch, with other digestible carbohydrates, being estimated by difference.

It appears that the proteids vary from 13 to 18, and the oil or fat from 7 to 12 per cent. In the two cases where the proteids reached 18 per cent., the proportions of both ash and indigestible fibre are also very large, as though the proportion of farinaceous substances to integument was smaller in these cases.

L. DE K.

Complete Analysis of Feeding Materials. By C. A. BROWNE, jun., and C. P. BEISTLE (*J. Amer. Chem. Soc.*, 1901, 23, 229—236).—The dried fodder is treated in succession with ether, boiling alcohol, cold water, solution of diastase, dilute sulphuric acid (1.25 per cent.), and dilute sodium hydroxide (1.25 per cent.), and the various dissolved and undissolved matters are estimated in the usual manner. The matter insoluble in sodium hydroxide is chlorinated for one hour and then again treated with alkali to remove condensed lignin. Pentosans are estimated in the original substance, and also in the residue from the chlorination process.

The authors have shown, by a series of experiments, that the pentosans pass to a large extent into the aqueous extract, and as they possess a decided cupric reducing power, it follows that they must greatly affect the accuracy of the estimation of dextrin. Another small quantity of pentosan is dissolved by the diastase treatment and slightly affects the accuracy of the estimation of starch. A large proportion of the pentosans is removed by the acid treatment. The furfuraldehyde-yielding constituents of the chlorinated fibre may perhaps not consist of true pentosans, but have an oxycellulose nature.

L. DE K.

Analysis of Soap. By PAUL BOHRISH (*Chem. Zeit.*, 1901, 25, 395—396).—After criticising various methods, the author recommends the following process. Moisture is estimated by drying 5 grams of soap shavings in an air-bath at 105°, the soap being first mixed with sand and a little alcohol, and the latter removed by heating on a water-bath. Ash is estimated by burning 5 grams of the sample and the sodium chloride contained therein is estimated by Volhard's silver process. The fatty

acids are estimated by heating 5 grams of the sample with 200 c.c. of water and 50 c.c. of $N/2$ sulphuric acid, the acids are collected on a weighed filter, well washed with hot water, and dried in a dish at 102° . They contain, however, the insoluble matters (fillings) and these are found by incineration. The filtrate is diluted to 500 c.c., and 100 c.c. are titrated with $N/10$ potassium hydroxide; the total alkali is thus obtained. To estimate free alkali, 5 grams of a soda soap or 30 grams of an olein soap are dissolved in hot absolute alcohol, the residue is well washed with the alcohol, and the filtrate is titrated with $N/2$ sulphuric acid. The residue is then dissolved in hot water, mixed with 50 c.c. of $N/2$ sulphuric acid, boiled, and the excess of acid titrated with $N/2$ potassium hydroxide; this gives the alkali carbonate.

L. DE K.

Apparatus for the simultaneous Estimation of Fat and Water in Butter. By HEINRICH PODA (*Zeit. Nahr. Genussm.*, 1901, 4, 492—496).—Eight c.c. of sulphuric acid of sp. gr. 1.64 are introduced into a specially constructed graduated tube, which is then placed for 5 minutes in a beaker containing boiling water, when the volume of acid is again carefully read. By means of a butter sampler, some of the butter to be tested is introduced into the tube; this is then stoppered, well shaken, and replaced in the beaker for 3 minutes. The tube is then whirled for 2 minutes in the Gerber apparatus. If no proper separation has taken place, the tube must be again shaken, replaced for 3 minutes in the boiling water, and again whirled. When a clear separation has taken place, the tube is finally placed for 4 minutes in the boiling water, and the volume of the two layers read off. The top layer is the butter, *minus* water and non-fatty substances; the bottom layer consists of the original sulphuric acid, *plus* the water and non-fatty matters of the butter. If the volume of the fatty layer be called f , and the increase of the acid w , then the percentage by weight of water, &c., in the sample will be found by dividing 100 by $1 + 0.848.f/w$. The percentage of fat is then found by deducting the result from 100. The results agree well with those found by gravimetric analysis.

L. DE K.

Butter control and the Reichert-Meissl Figure. By MORITZ SIEGFELD (*Zeit. Nahr. Genussm.*, 1901, 4, 433—446).—A lengthy record of authenticated cases of genuine butters where the Reichert-Meissl number fell below the recognised standard.

L. DE K.

Causes of the varying Composition of Butter. By J. J. L. VAN RYN (*Landw. Versuchs-Stat.*, 1901, 55, 347—378).—Physical and chemical constants were determined in a large number of samples of butter obtained during different months. It was found that feeding in stalls as compared with pasture had a considerable effect on the composition of the butter. Whilst in Limburg and North Brabant no samples of butter showed abnormal values (never lower than 28) for the saturation numbers of the volatile fatty acids at the end of October and the beginning of November, samples from more northern parts of Holland, where the cows are kept on pasture until late in the autumn, only rarely gave numbers as high as 28.

Chemical and physical examinations of butter are insufficient to show whether the sample is pure, unless the results greatly exceed the limits usually adopted, or unless the presence of margarine can be qualitatively established.

N. H. J. M.

Baudouin's Reaction for the detection of Sesamé Oil, and Tambon's Modification of the Test. By F. UTZ (*Chem. Zeit.*, 1901, 25, 412—413. Compare Abstr., 1900, ii, 699).—A review of the many modifications of Baudouin's hydrochloric acid and sugar test for sesamé oil proposed from time to time.

The author cannot recommend the latest modification proposed by Tambon (this vol., ii, 360). Soltsien's reaction with stannous chloride (Abstr., 1900, ii, 325) seems to give the most trustworthy results.

L. DE K.

Sunflower Oil. By FERDINAND JEAN (*Ann. Chim. anal. appl.*, 1901, 6, 166—167).—This oil, according to the author, is palatable, well adapted for burning in lamps, and also has considerable drying properties; for soap making, it is not so well adapted.

The following properties are given, sp. gr. 0.925, refraction in oleorefractometer + 22°, saponification number 192, iodine absorption 124, critical temperature of solution in 94 per cent. alcohol 104°, melting point of fatty acids 22°, unsaponifiable matter (phytosterol) 0.72 per cent., acidity as oleic acid 3.102, solubility in alcohol 0.6 per cent. With a drop of sulphuric acid, a persisting golden-yellow spot is obtained, surrounded by a greyish-blue zone, fringed with clear, brownish spots; this is a very characteristic test for the oil. The oil reduces an alcoholic solution of silver nitrate, but is not affected by Halphen's sulphur reagent or by a mixture of sugar and hydrochloric acid.

L. DE K.

Approximate Estimation of Formaldehyde in Milk. By JOHN F. LIVERSEEGE (*Analyst*, 1901, 26, 151—152).—The reagent consists of a mixture of 100 c.c. of sulphuric acid and 2.5 c.c. of normal ferric chloride, which, as is well known, causes the formation of a violet-blue ring when added to milk containing formaldehyde. Ten c.c. of the suspected sample are put into a 25 c.c. stoppered cylinder, and the reagent is added 1 c.c. at a time, until a violet colour appears and does not increase in intensity. By making experiments side by side with samples containing a definite proportion of formaldehyde, a fair idea as to the percentage may be obtained as the violet-colour appears the sooner the more formaldehyde is present.

L. DE K.

Detection and Estimation of Preservatives in Milk. By MEREDITH WYNTER BLYTH (*Analyst*, 1901, 26, 148—150).—Ten c.c. of the suspected samples are put into clean, wide test-tubes, and into another tube are put 10 c.c. of a sterilised milk free from preservatives. To each milk are added 2 c.c. of a very strong, slightly alkaline solution of litmus, and if any of them should show an acid reaction, this is remedied by cautiously adding $N/2$ sodium hydroxide. After plugging the tubes with cotton-wool they are heated for 10 minutes in a water-bath at 80°, and when cold are each inoculated with 0.5 c.c. of a

mixture of 0.5 c.c. of sour milk and 100 c.c. of water. After thoroughly shaking, the tubes are kept for 24 hours at any temperature between 15° and 25° and then examined. Those tubes which contain preservatives will remain blue or pink, whilst those containing no preservatives will behave in the same way as the pure sample and become white, or nearly so. The length of time the colour takes to fade depends on the nature and quantity of the preservative added. 0.005 per cent. of borax, boric acid, or mixtures of these substances, 0.05 per cent. of salicylic acid, and 0.0003 per cent. of formaldehyde may be detected by this process; their exact nature must, of course, be determined by the ordinary methods.

As regards the determination of the amount of the preservative, this, in the case of borates or salicylic acid, is best effected by the usual chemical methods, but for formaldehyde the bacteriological process is best adapted. Into each of two test-tubes is introduced 10 c.c. of the sample (solutions A). Another 10 c.c. is diluted to 100 c.c. with milk free from preservatives, and 10 c.c. of the mixture is put into each of another two test-tubes (solutions B). Ten c.c. of solution B are diluted to 100 c.c. with milk free from preservatives, and 10 c.c. of this is put into two tubes (solutions C). Three control tubes are prepared of 10 c.c., each containing 0.005, 0.003 and 0.001 per cent. of formaldehyde respectively (control A). Four control tubes are prepared of 10 c.c., each containing 0.001, 0.0008, 0.0005, and 0.0003 per cent. of formaldehyde respectively (control B). All the tubes are coloured with litmus, heated to 80°, allowed to cool, and inoculated in the manner described. One tube of A, one of B, one of C, and the three control solutions A are placed in the warm incubator at 22° for 24 hours, and all the other tubes are placed in the cold incubator for 24 hours. From a comparison of the colours, a very close approximation may then be made to the quantity of formaldehyde originally present in the milk, providing that quantity does not exceed 0.5 per cent., in which case still larger dilutions should be made.

L. DE K.

Spectral Reactions of Methylfurfuraldehyde. By KINTARO OSHIMA and BERNHARD TOLLENS (*Ber.*, 1901, 34, 1425—1426).—Widtsoe and Tollens (*Abstr.*, 1900, i, 244) have shown that the presence of methylpentoses or methylpentosans in a substance may be detected by distilling with hydrochloric acid of sp. gr. 1.06, mixing the distillate with an equal volume of concentrated hydrochloric acid, and examining the absorption spectrum of the liquid. If methylfurfuraldehyde is present, dark bands are seen between the green and blue, the violet also being darkened although remaining distinctly visible. It is now found that this reaction becomes more sensitive in presence of phloroglucinol, and that the test is conveniently carried out as follows. About 5 c.c. of the hydrochloric acid distillate are mixed in a test-tube with an equal volume of concentrated hydrochloric acid, and a solution of phloroglucinol in hydrochloric acid of sp. gr. 1.06; after about 5 minutes, the liquid is filtered to remove any furfuraldehyde phloroglucide and examined spectroscopically.

T. H. P.

Detection of Acetanilide in Urine. By A. PETERMANN (*Ann. Chim. anal. appl.*, 1901, 6, 165. Compare this vol., ii, 293).—Ten c.c. of cows' urine are mixed with 25 c.c. of strong hydrochloric acid and boiled for a few minutes. When cold, 1 c.c. of a 3 per cent. aqueous solution of phenol is added and then, after shaking, 2 or 3 drops of a 10 per cent. solution of bleaching powder, shaking after the addition of each drop; as much as six drops may be added if no reaction is at first obtained. In the presence of *p* aminophenol, a product of decomposition of acetanilide, the urine assumes a red colour, but as this may be simply due to the action of the acid on the urine itself, the liquid is made alkaline with ammonia, which should turn the colour to blue. In the presence of much acetanilide the reaction is safe, but otherwise somewhat doubtful; a further confirmatory test should therefore be made. 100—200 c.c. of the suspected urine are mixed with 25—50 c.c. of hydrochloric acid and boiled for some minutes. When cold, the liquid is neutralised with calcium carbonate and extracted several times with ether. The ether is then shaken with dilute hydrochloric acid (1:3), the acid liquid is warmed to expel any ether, and then treated as directed with phenol, bleaching powder, and ammonia. The reaction will then be very distinct.

L. DE K.

Microchemical Investigation of Alkaloids. By M. E. Pozzi-Escot (*Compt. rend.*, 1901, 132, 1062).—When viewed under the microscope, strychnine platinichloride presents the appearance of starlike aggregates of pink, flattened prisms, its aurichloride forms aggregated prisms, and the compound produced with potassium iodide separates in well-defined sheaves of olive-green crystals.

Brucine platinichloride forms acicular prisms.

Quinine platinichloride separates in small, anisotropic granules, whilst its potassium periodide forms microscopic prisms.

Cocaine platinichloride forms serrated crystals consisting of aggregates of prismatic needles; its aurichloride separates in serrated crystals grouped in arborescent clusters.

Codeine, when treated with mercuric iodide dissolved in potassium iodide, yields rosettes of almost black crystals.

Atropine when treated with iodine dissolved in potassium iodide, yields an abundant crop of black, acicular crystals exhibiting external twinning; morphine under these conditions furnishes crystals separating in clusters resembling thistle flowers.

G. T. M.

Evaluation of Medicinal Drugs containing Alkaloids. By HARRY M. GORDIN (*Arch. Pharm.*, 1901, 239, 214—231).—The amount of alkaloid present in various drugs was determined by the author's method (*Abstr.*, 1900, ii, 119, 777), the alkaloid being extracted thoroughly with a suitable solvent, and the residue examined further to ensure that the extraction was complete. This method is too tedious for ordinary use, however; the results given by it were used as a standard with which those obtained by more expeditious methods were compared and judged. Of these methods, two were employed: (A), 10—20 grams of the powdered drug were extracted for 2—4 hours with boiling 95 per cent. alcohol in Dunstan and Short's apparatus (*Pharm. J.*, [iii], 13, 664). The alcoholic extract

was concentrated by distillation on the water-bath to about 10 c.c., cooled, and diluted to 50 or 100 c.c. with water slightly acidified, shaken well with about 1 gram of pure, powdered talc, and filtered. An aliquot portion of the filtrate was made alkaline with a suitable alkali, and the alkaloid extracted by shaking three or four times in succession with a suitable mixture of ether or chloroform. If ammonia had been used, the solvent was simply distilled off; if a fixed alkali, it was first shaken with a little calcined magnesia, filtered through a dry filter, and then distilled. The residue was dissolved in an excess of standard acid, and the alkaloid estimated by the author's method. The method A is rapid and easy, and it is cheap because all the solvents are recovered. (B) 10—20 grams of the drug, very finely powdered, were digested for 6—12 hours with frequent shaking with 10—15 times their weight of modified Prollius' liquid (28 per cent. ammonia, 10 c.c.; alcohol, 25 c.c.; chloroform, 80 c.c.; ether, 250 c.c.). When the liquid had cleared, an aliquot part was removed with a pipette; this was either shaken with water slightly acidified, or the solvent was distilled off from it, and the residue dissolved in dilute acid. The aqueous solution was then made alkaline, extracted with ether-chloroform, &c., as in the other method. This method is very like Keller's, but avoids the use of water, which introduces uncertainty into the results. With coca leaves and *Hydrastis canadensis*, method A should be used; it gives results identical with those obtained by the standard method. With cinchona bark, method B gives correct results, both for total alkaloids and those soluble in ether; it should also be used with *Nux vomica*, although the results are slightly low in this case; and with ipecacuanha, for although the results are low when the factor used is calculated from the formula $C_{30}H_{40}O_5N_2$ of (dibasic) emetine, correct results can be obtained by using an empirical factor, namely, 1 c.c. $N/40$ acid = 0.0066 gram emetine.

Hemlock is assayed by shaking vigorously 20 grams of the finely powdered leaves or seeds with a mixture of ether and chloroform (3:1), adding 10 c.c. of 10 per cent. aqueous sodium hydroxide, and shaking for 4 hours. When the liquid has cleared, 100 c.c. are removed with a pipette, mixed with 10 c.c. of 2 per cent. alcoholic oxalic acid, and evaporated on the water-bath, air being blown through the flask finally to remove the last traces of liquid. The residue is then treated with 10 c.c. of absolute alcohol and filtered into a beaker, the filter and undissolved ammonium oxalate being washed with absolute alcohol. The filtrate is concentrated on the water-bath to 2—3 c.c., mixed with 10 c.c. of water, and diluted with water to 25 c.c. in a small graduated flask, shaken vigorously with a little talc, and filtered through a dry filter. Of the filtrate, 12.5 c.c. (= 5 grams of the drug) are removed with a small pipette to a separating funnel, and mixed with excess of 10 per cent. aqueous sodium hydroxide; the alkaloid is extracted by shaking three times with light petroleum (distilling below 60°, without residue), 25 c.c. being used each time. The extract is shaken for about 10 minutes with about half a gram of calcined magnesia, filtered, the residue and filter being washed with light petroleum, the filtrate mixed with 50 c.c. of a saturated solution of hydrogen chloride in dry ether and distilled to dryness, air being

blown through the flask finally. The residue is mixed with 25 c.c. of $N/40$ silver nitrate, and about 5 c.c. of 10 per cent. nitric acid, diluted to 100 c.c. when the silver chloride has settled, filtered, and 50 c.c. of the filtrate mixed with about 5 c.c. of iron alum solution, and titrated with $N/40$ potassium thiocyanate. The c.c. of $N/40$ silver nitrate used per 5 grams of the drug are multiplied by 0.0635, and the result is the percentage of alkaloid in the drug, calculated as coniine.

The estimation of the total alkaloids in the fluid extract of cinchona has been described already (Abstr., 1900, ii, 777). For the estimation also of the alkaloids soluble in ether, 10 c.c. of the extract are diluted to 50 (or 100) c.c. with 2 per cent. sulphuric acid, shaken with a little talc, and filtered through a dry filter; 50 c.c. of the filtrate (= 5 c.c. of the extract) are made strongly alkaline with aqueous sodium hydroxide, and shaken three times with ether-chloroform (3 : 1). The extract is shaken with a little calcined magnesia, filtered into a tared flask, and the total alkaloids determined gravimetrically, those soluble in ether volumetrically, either $N/20$ or $N/10$ acid being used to take up the latter.

C. F. B.

Volumetric Estimation of Morphine by means of Potassium Iodate and Arsenious Acid in Alkaline Solution. By C. REICHARD (*Chem. Zeit.*, 1901, 25, 328—329).—The solution containing the morphine salt is mixed with potassium iodate and dilute sulphuric acid, and the liberated iodine extracted by repeated agitation with carbon disulphide or chloroform. The extract is then mixed with solution of potassium iodide, and gently heated on the water-bath until the carbon disulphide or chloroform has evaporated. The remaining iodine solution (if preferred, the original solution in carbon disulphide or chloroform may be taken) is mixed with excess of standard arsenious acid, and the excess of arsenic titrated with standard iodine, with the usual precautions. One atom of iodine liberated is equivalent to 3 mols. of morphine.

The author is engaged in estimating morphine by means of an ammoniacal solution of silver chloride (compare this vol., ii, 140).

L. DE K.

Detection of Indican in Urine containing Iodides. By A. KUHN (*Chem. Centr.*, 1901, i, 800—801; from *Münch. med. Woch.*, 48, 52).—For urine containing iodides, Obermayer's ferric chloride and hydrochloric acid test is preferable to Jaffé's method, as it is somewhat less sensitive to iodides, not being affected by 1 part of potassium iodide in 10,000, whilst Jaffé's method and the starch reaction will both show that amount. Neither reagent will detect 1 part of iodide in 100,000. The use of sodium thiosulphate is recommended as a means of discriminating between iodine and indican, but no details are given.

M. J. S.

Estimation of Urinary Indican as Indigo-Red by means of Isatin and Hydrochloric Acid. By JACOB BOUMA (*Zeit. physiol. Chem.*, 1901, 32, 82—93. Compare Abstr., 1900, ii, 700).—The following method is recommended for the estimation of indoxyl in urine. The urine is first treated with lead acetate (1 vol. to 10 vols. of urine) and the clear filtrate mixed with its own volume of isatin

solution (20 grams in 1 litre of concentrated hydrochloric acid). The mixture is warmed on the water-bath for 15 minutes, cooled, extracted with chloroform, the chloroform evaporated, and the residue dried at 110° ; this residue is extracted with boiling water to remove any excess of isatin, again dried, treated with sulphuric acid, and then titrated with potassium permanganate which has been standardised by the aid of pure indigo-red. For the titration, the amount of indigo-red should not be less than 1 in 20,000, and the solution must be perfectly clear. The amount of indigo found is double that which would have been given by the indoxyl alone, as one mol. of isatin condenses with one mol. of indoxyl to yield indigo. A colorimetric method for the estimation of urinary indican for clinical purposes is also described.

J. J. S.

New Reaction of "Saccharin" (*o*-Benzoicsulphinide). By ALEXANDRE LEYS (*Compt. rend.*, 1901, 132, 1056—1058).—A warm, dilute solution of hydrogen peroxide containing a trace of a copper or ferric salt produces an intense brown coloration and precipitate with organic compounds containing unsaturated rings; this reaction takes place with benzene, pyrrole, thiophen, furfuraldehyde, antipyrine, "saccharin," acetanilide, *o*-phenylenediamine hydrochloride, benzoic and cinnamic acids, and the phenols and their carboxy-derivatives, negative results being obtained with alcohol, sucrose, allyl acetate, menthol, turpentine, and acetic, lactic, and fumaric acids. In the case of "saccharin," the addition of a mineral acid prevents the formation of the brown compound, a trace of acid removes the yellow tint of the coloration, and when the reaction is carried out in the cold, a violet coloration slowly develops constituting a very delicate test for the sweetening principle. Milk is examined for "saccharin," after precipitating the casein by means of potassium hydrogen sulphate and alcohol, by extraction with ether, removal of the solvent by evaporation and examination of the residue dissolved in water by means of cold dilute solutions of hydrogen peroxide and ferric chloride. Butter is treated with a mixture of chloroform, alcohol, and water, and the dilute alcoholic extract examined as in the preceding example; the violet coloration produced should not appear on the addition of ferric chloride, but only after the introduction of hydrogen peroxide.

G. T. M.

Cell for the Clinical Determination of Hæmoglobin in Urine. By PAUL ADAM (*Bull. Soc. Chim.*, 1901, [iii], 25, 607—608).—A short account of a glass cell for the spectroscopic examination of liquids; it is made in a mould, the exterior faces being afterwards planed and polished.

N. L.

Colorimetric Estimation of Hæmoglobin. By JOHN S. HALDANE (*J. Physiol.*, 1901, 26, 497—504).—Hæmoglobin can be easily and accurately estimated in terms of its oxygen capacity, by means of a standard solution of carbonic oxide hæmoglobin. The standard is permanent when properly sealed. The Gowers' hæmoglobinometer provided with this standard gives good results. The average oxygen capacity of the blood is 18.5 per cent. in adult healthy men, 16.5 in women, and 16.1 in children.

W. D. H.

General and Physical Chemistry.

Molecular Refraction of Chloral Hydrate in Solution in various Solvents. By MAX RUDOLPHI (*Zeit. physikal. Chem.*, 1901, 37, 426—447).—From the results of an examination of chloral hydrate in solution in water, alcohol, or toluene, no preference can be given to any of the four formulæ which have been suggested for determining molecular refraction from the refractive index. The refraction deduced from the aqueous and alcoholic solutions agrees well with that calculated from the atomic refractions, but not so well with the observed refraction of superfused chloral hydrate. Observations in toluene lead to a considerably higher molecular refraction. The solvent, therefore, may exert a great influence on the refraction, and this cannot be traced to electrolytic dissociation. Toluene has nearly the same index of refraction as chloral hydrate, and yet is the most anomalous of the solvents used, and this confirms Brühl's observation (*Abstr.*, 1897, ii, 129) that optical similarity is no guide as to the usefulness of a particular solvent for the determination of the refraction of the dissolved substance. J. McC.

Arc Spectrum of Vanadium. By SIR NORMAN LOCKYER and F. E. BAXANDALL (*Proc. Roy. Soc.*, 1901, 68, 189—210. Compare Hasselberg, *Abstr.*, 1900, ii, 381).—The sources of the spectra were (1) vanadium chloride, (2) vanadium oxide, each volatilised between poles of pure silver. A full list of the lines is given and compared with the lists of Rowland and Harrison, and Hasselberg. The authors have detected 194 lines that do not appear in either of these lists.

J. C. P.

Triboluminescence. By L. TSCHUGAEFF (*Ber.*, 1901, 34, 1820—1825).—Triboluminescence denotes the property possessed by some crystalline substances of becoming luminous when rubbed or struck (compare Wiedemann, *Ann. Phys. Chem.*, 1888, [ii], 34, 446). The author has subjected about 500 organic and inorganic substances to these conditions, and found that 25 per cent. (chiefly organic) show this behaviour. The property seems peculiarly associated with ring compounds, and the intensity of the light emitted is greatest in these cases; certain groups, namely, hydroxyl, carbonyl, and secondary or tertiary nitrogen, specially favour the production of triboluminescence. Of the alkaloids or alkaloid salts investigated, 65 per cent. possess the property. The substances examined are divided into classes, accordingly as the intensity of the light emitted is approximately that of (1) uranium nitrate, (2) tartaric acid, or (3) ammonium oxalate. Triboluminescence of the first degree is exhibited by uranium nitrate, quinine valerate, cocaine salicylate, cinchonamine, coumarin, and aniline hydrochloride. The colour of the light emitted varies with the substance examined, and the luminosity generally lasts only so long as external force is applied; in certain cases, however, such as acetanilide and sulphanilic acid, the luminosity lasts longer. The author's

results point to a close connection between triboluminescence and optical activity (compare Andreocci, Abstr., 1899, ii, 719).

J. C. P.

Contact Electromotive Forces and the Theory of Ions. By E. ROTHÉ (*Compt. rend.*, 1901, 132, 1478—1481).—A Lippmann electrometer was employed, and the *E.M.F.*'s necessary to obtain the maximum height of the mercury in the electrometer were determined, the solutions employed being saturated solutions of mercurous chloride and sulphate in hydrochloric and sulphuric acids of varying concentrations. The *E.M.F.* was found to increase with the concentration of the acid, a result in accord with the theory of Nernst, and values of the *E.M.F.* calculated by Nernst's formula agree well with the experimental determinations.

L. M. J.

Electromotive Relations of Compounds with several Oxidation Stages. By E. ABEL (*Zeit. physikal. Chem.*, 1901, 37, 623—625).—A discussion of some of the results obtained by Luther (this vol., ii, 301).

L. M. J.

Electrical Conductivity of Air and Salt Vapours. By HAROLD A. WILSON (*Proc. Roy. Soc.*, 1901, 68, 228—230. Compare Abstr., 1899, ii, 722).—The relation between the current and the *E.M.F.* in air depends very much on the direction of the current, namely, whether the outer electrode is positive or negative. With salt vapours, the relation between current and *E.M.F.* is not much affected by reversing the current; at low temperatures, the current attains a saturation value, but above 1000° it increases more nearly in proportion to the *E.M.F.*

For air, the relation of current and temperature at constant *E.M.F.* may be expressed by a formula of the type $C = A\theta^n$, where C is the current, θ the absolute temperature, A and n constants, the value of n depending on the *E.M.F.* used. The energy required to ionise 1 gram-mol. of air between 1000° and 1300° is estimated to be 60,000 cal.

For salt vapours, the relation between current and temperature is complicated; the current shows a maximum value about 900°, and increases very rapidly about 1150°. The energy required to ionise 1 gram-mol. of potassium iodide is estimated to be 15,000 cal. at about 300°.

The maximum current carried by the salt vapour (at 1300° and 800 volts) is nearly equal to that required to electrolyse the same amount of salt in solution—a fact in favour of the view that the ions are of the same nature in the two cases.

J. C. P.

Electrical Conductivity in Gases exposed to the Action of Cathode Rays. By J. C. McLENNAN (*Zeit. physikal. Chem.*, 1901, 37, 513—545).—The conductivity of gases under the influence of cathode rays may be completely explained on the hypothesis that positive and negative ions are produced in the gas. By the action of cathode rays on an insulated conductor, positive charges are completely dissipated, whilst uncharged or negatively electrified conductors

retain a residual negative charge. In the author's experiments, the effects are due, not to the Röntgen, but to the cathode rays. Methods for the determination of the extent of the ionisation in gases are considered, and experiments with air, nitrogen, carbon dioxide, hydrogen, and nitric oxide show that the ion concentration with constant cathode rays is proportional to the density of the gas and independent of its chemical nature. Ionisation in the same gas at different pressures is similarly proportional to the pressure, whilst in all cases it is further shown that the ionisation is directly proportional to the energy absorbed.

L. M. J.

Degree of Dissociation and Dissociation Equilibrium in the case of Highly Dissociated Electrolytes. By HANS JAHN (*Zeit. physikal. Chem.*, 1901, 37, 490—503. Compare Abstr., 1900, ii, 707).—Provided that $C^2/(c - C) = \text{const.}$, where c is the total concentration and C the concentration of the free ions, then Nernst's formula for the calculation of the *E.M.F.* of a concentration cell can be derived from the exact formula of Arrhenius. The author finds, from results of Loomis (Abstr., 1896, ii, 352), Hausrath (*Inaug. Diss. Göttingen*, 1901), and Abegg (Abstr., 1896, ii, 587), that for the chlorides and nitrates of potassium, sodium, and ammonium, $C^2/(c - C) \cdot \lambda^{-c} = \text{const.}$ (λ being a constant for each substance). As the concentration decreases, the value of λ^{-c} approaches unity, and therefore for very dilute solutions $C^2/(c - C) = \text{approx. const.}$ Nernst's formula is only accurate when dilute solutions are employed in the cell, but even when the solutions are concentrated, the formula introduces only a very small error, and one quite incapable of explaining the large deviation between the experimentally determined *E.M.F.* and that calculated with the aid of μ/μ_∞ for various concentration cells.

The author suggests that the apparent inapplicability of the law of mass action to solutions of strong electrolytes may be due to an influence which charged ions exert on each other, there being no such influence between neutral molecules at high dilution. J. McC.

Electrically Heated and Electrically Controlled Thermostat. By STEWART W. YOUNG (*J. Amer. Chem. Soc.*, 1901, 23, 327—330).—The author has devised an electrical thermostat in which the heating is effected by incandescent lamps and regulated by a modification of the ordinary gas regulator; by means of this apparatus, the temperature can be maintained within 0.02—0.03 of a degree. For details, the description and diagram in the original must be consulted.

E. G.

Gradual change of Glass and the variation of the Zero point of Thermometers. II. Accurate Thermometry. By L. MARCHIS (*Zeit. physikal. Chem.*, 1901, 37, 553—604; 605—612).—The first paper is an extension of the author's previous paper on this subject (Abstr., 1899, ii, 545), whilst in the second paper the application of the results obtained to thermometry are discussed. The usual precautions observed are theoretically justified, but it is shown that multiplicity of alternate heating and cooling is unnecessary for bringing the thermometer to the natural state. A precaution of the utmost

importance is the maintenance of the thermometer at a temperature close to that of the experiments during the intervening periods.

L. M. J.

Specific Heats of Alloys. By DOMENICO MAZZOTTO (*Nuovo Cimento*, 1901, [v], 1, 355—357).—The discordance between the numbers given by Spring and by the author for the specific heat of Lipowitz's alloy, recently referred to by van Aubel (*J. de Physique*, [iii], 1900, 9, 493), is due to the different behaviour of the alloy according as it is previously heated above or below its melting point. In the former case, widely differing values are obtained for the specific heat for various ranges of temperature, whilst in the latter case the different numbers vary only from 0.0351 to 0.0359, the mean value being 0.0354.

T. H. P.

Latent Heats of Evaporation of some Organic Nitrogenous Compounds. By LOUIS KAHLENBERG (*J. Physical Chem.*, 1901, 5, 284—288).—The specific heats and latent heat of evaporation were determined for amylamine, dipropylamine, diisobutylamine, valeronitrile, and α -picoline. The results obtained were:

| Compound. | Specific heat. | Latent heat. | ML/T. |
|--------------------------|----------------|--------------|-------|
| Amylamine..... | 0.6136 | 98.75 | 23.3 |
| Dipropylamine | 0.5972 | 75.69 | 20.0 |
| Diisobutylamine..... | 0.5706 | 65.85 | 20.8 |
| Valeronitrile | 0.5199 | 95.95 | 19.8 |
| α -Picoline | 0.4342 | 90.75 | 21.0 |

The value of Trouton's constants appears to indicate a certain amount of association in the molecules of amylamine, but simple molecules in case of the other compounds (compare Abstr., 1898, ii, 269).

L. M. J.

Phosphorus Oxychloride as a Solvent in Cryoscopy. By GIUSEPPE ODDO (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 452—458).—The mol. depression of the freezing point of phosphorus oxychloride is found by measurements with solutions of toluene, sulphur monochloride, and bromine to have the value 69; tetrachloromethane gives a slightly higher number. In dilute solution in phosphorus oxychloride, aniline hydrochloride, pyridine hydrochloride, ferric chloride, platinum tetrachloride, and gold trichloride all undergo dissociation, giving approximately half the calculated molecular weights.

T. H. P.

Freezing Point of Aqueous Solutions of Non-electrolytes. II. By ELMER H. LOOMIS (*Zeit. physikal. Chem.*, 1901, 37, 407—425. Compare Abstr., 1900, ii, 335).—The zero point of the thermometer which has been in use in this investigation during the past seven years has constantly risen. The rise was continuous, and so slow as to be without influence on the results; only in one instance was a sudden change (from $+0.0538^\circ$ to $+0.0521^\circ$) observed.

The non-electrolytes investigated were lactose, maltose, l  vulose, dulcitol, acetamide, and salicin. The mol. depression (calculated from m , the number of gram-mol. per 1000 c.c. of solution) increases regularly

with rise of concentration from $m = 0.01$ to $m = 0.2$. If the mol. depression (corrected mol. depression) be calculated from m' , the number of gram-mol. of dissolved substance in 1000 grams of water, it is found to remain constant for all concentrations of lævulose (1.86), and dulcitol (1.85), as well as for methyl and ethyl alcohols, dextrose, mannitol, glycerol, and chloral hydrate previously examined; it increases gradually, with increasing concentration, in the cases of lactose (1.86 to 1.88), and maltose (1.86 to 1.89), as well as of sucrose; it exhibits a continuous diminution for acetamide (1.83 to 1.81) and salicin (1.86 to 1.84), *n*-propyl, *n*-butyl, and amyl alcohols, acetone, and aniline.

The fact that molecular solutions of a large number of non-electrolytes at high dilution have the same freezing point shows that they have also the same osmotic pressure, and consequently Avogadro's hypothesis is strictly applicable to dilute solutions. It is shown that as in many cases the corrected mol. depression remains constant over a wide range of concentration, van't Hoff's assumption that the osmotic pressure follows the laws of Boyle and Gay-Lussac is correct. An analogy is drawn between those substances for which the corrected molecular depression does not remain constant and gases which do not obey Boyle's law.

From results with aniline and many other aromatic substances, it is concluded that benzene compounds exist in aqueous solution in the form of molecular aggregates, and that the association of these increases with the concentration.

As in no case does the mol. depression at great dilution exceed 1.86, there is no evidence of the slightest dissociation of any non-electrolyte examined.

J. McC.

Molecular Depression of the Temperature of Maximum Density of Water produced by the dissolution of Chlorides, Bromides, and Iodides of the Alkali Metals. By LOUIS C. DE COPPET (*Compt. rend.*, 1901, 132, 1218—1220).—It was found that the depression is approximately proportional to the quantity of dissolved salt, and that the molecular depression is hence approximately constant, the value differing, however, for different salts, as seen in the following table:

| | Chloride. | Ratio. | Bromide. | Ratio. | Iodide. |
|-----------------|-----------|--------|----------|--------|---------|
| Rubidium | 11.7° | 0.89 | 13.2° | 0.85 | 15.6° |
| Potassium | 11.6 | 0.91 | 12.8 | 0.83 | 15.4 |
| Sodium | 13.2 | 0.91 | 14.5 | 0.85 | 17.0 |
| Lithium | 6.0 | 0.86 | 7.0 | 0.84 | 8.3 |
| Ammonium..... | 7.2 | 0.83 | 8.7 | 0.78 | 11.1 |

The ratio of the depressions produced by chlorides and bromides, or iodides, is approximately independent of the metal (*Abstr.*, 1899, ii, 590).

L. M. J.

Connection between Surface Tension and Solubility. By GEORGE A. HULETT (*Zeit. physikal. Chem.*, 1901, 37, 385—406).—Precipitates, when first formed, consist of very small particles which gradually become larger, the growth taking place by the solution of the smallest particles. In this way, the solution becomes supersaturated

with respect to larger particles, and there is, consequently, deposition of solid on the larger particles. Ostwald has shown that this is due to surface energy, which tends to a minimum.

This necessitates that the solubility of a solid should be dependent upon the state of division of the solid with which the solution is in contact. Experiments with calcium sulphate have confirmed this, as it has been found that variation in the size of the particles employed for solution leads to variations in the concentration, which can be detected by conductivity determinations. A normally saturated solution of gypsum at 25° contains 2.085 grams of calcium sulphate per litre, the size of the particles being not less than 2μ ($\mu = 0.0001$ cm.). If the particles are smaller (0.3μ), the concentration of the saturated solution rises to 2.476 grams of calcium sulphate per litre. The concentration of this latter solution quickly falls to the lower concentration, and the particles increase in size. The same relationships were found with barium sulphate; the saturated solution has the concentration 2.29 mg. per litre at 25° ($\mu = 1.8$), but when $\mu = 0.1$, the solution contains 4.15 mg. per litre. By still further reducing the size of the particles, the solubility was increased by 20 per cent.

Ordinary coarse mercuric oxide is soluble to the extent of 50 mg. per litre at 25°, but when very finely powdered the solubility increases to 150 mg. per litre (determined colorimetrically).

The author has also calculated the surface energy between solid and solution.
J. McC.

Internal Friction of Solutions of Chrome Alum. By EPISIO FERRERO (*Nuovo Cimento*, 1901, [v], 1, 285—287).—In order to determine whether the change in colour from reddish-violet to green produced in chrome alum solution by heating is accompanied by an alteration in the internal friction of the liquid, the author has measured the latter magnitude for two solutions containing respectively 20.5 and 13.75 per cent. of the alum. In each case, the liquid was heated to a certain temperature, then cooled to 20.5°, and the measurement made at this temperature. The numbers obtained show that the internal friction of chrome alum solutions begins to undergo a gradual diminution when heated to about 55°, a temperature corresponding approximately with the change in colour from violet to green; this diminution continues until the temperature reaches about 80°, above which the internal friction has a constant value. The difference between the values of the internal friction for the green and violet solutions diminishes with the concentration.
T. H. P.

Influence of Acids on the Solubility of Salts containing the same Ion. By J. E. ENKLAAR (*Rec. Trav. Chim.*, 1901, 20, 183—197).—The solubility of sodium chloride in water containing various quantities of hydrochloric acid at 10° and 10.5° has been determined. Assuming that these two electrolytes are dissociated to the same extent, the solubility of the sodium chloride should be expressed by $m = -x/2 + \sqrt{m_0^2 + x^2/4}$, x being the concentration of the hydrochloric acid and m_0 being the solubility of sodium chloride in pure water; this follows from the assumption that the product of the con-

centrations of sodium and chlorine ions is constant. The solubility found is always less than that calculated, and the difference is proportional to the amount of hydrochloric acid present. The sum ($x + m$) is almost constant and equal to m_0 . The diminution of the solubility is possibly to be explained by the contraction which the water suffers by the presence of the free ions of the hydrochloric acid.

Similar relationships have been found at 27° and 41° , and also with barium chloride in hydrochloric acid and barium nitrate in nitric acid. The solubility of sodium acetate is hardly affected by the presence of acetic acid. J. McC.

Catalysis. III. Theory of Contact Action. By HANS EULER (*Öfver. K. Vetens. Akad. Förhandl.*, 1900, 57, 267—276).—In earlier papers, the author has enunciated the principle that in every case of catalysis there is an increase in the number of the ions concerned in the reaction. It is now shown how this principle applies in the case of contact action, especially in that of platinum catalysis. All reactions accelerated by platinum are oxidation or reduction processes, and the author connects the catalytic effect of platinum black with its great power of absorbing and retaining oxygen and moisture (compare Mond, Ramsay, and Shields, *Abstr.*, 1895, ii, 492). When platinum black is carefully reduced by gently warming in a current of hydrogen, its catalytic effect on the decomposition of hydrogen peroxide is seriously impaired. Bredig and Müller von Berneck (*Abstr.*, 1900, ii, 213) have shown that the reaction $\text{H}_2\text{O}_2 + \text{O} = \text{H}_2\text{O} + \text{O}_2$ is monomolecular, whence it follows that oxygen atoms take part in the reaction, and that their concentration remains constant. The ionisation of the oxygen at the surface of the platinum is to be attributed to the presence of water and to the high absorption pressure. J. C. P.

Catalysis of Electrolytic Gas by Colloidal Platinum. By CARL ERNST (*Zeit. physikal. Chem.*, 1901, 37, 448—484).—Bredig's colloidal platinum solution exerts a catalytic influence on electrolytic gas, and the product is quite free from ozone and hydrogen peroxide. The diminution in the gas volume per unit of time is directly proportional to the absolute amount of platinum in the solution and to the concentration (pressure) of the gas mixture. If hydrogen and oxygen be mixed in proportions other than 2:1, the excess of one of the gases appears to act merely as a diluent. A satisfactory constant has been found for $k = C \cdot \Delta t / \Delta v$, where C is the concentration of the mixture ($2\text{H}_2 + \text{O}_2$), Δt the time interval, and Δv the diminution in volume.

The author believes that the reaction may be accounted for in the same way that Bodenstein (unpublished) explains the catalysis of electrolytic gas by platinum foil: the assumption made is that the diminution in volume measures the rate of absorption of the two gases by the platinum which thereafter combine, but this diminution does not measure the rate of combination of the hydrogen and oxygen.

Finally, it has been shown that those substances which "poison" colloidal platinum solution for the decomposition of hydrogen peroxide (Bredig and Müller von Berneck, *Abstr.*, 1900, ii, 213; Bredig and

Ikeda, this vol., ii, 441) exert a similar retarding effect on the catalysis of electrolytic gas. J. McC.

The Paralysing of Platinum Catalysis by "Poisons." By ROBERT W. RAUDNITZ (*Zeit. physikal. Chem.*, 1901, 37, 551—552).—It is shown that the catalytic decomposition of hydrogen peroxide, which is hindered by the addition of hydrocyanic acid, takes place with undiminished energy if the acid is removed by blowing a current of air through the liquid, so that the catalyst has not been affected. The effect of the "poison" is probably analogous to that of those compounds which diminish the luminosity of phosphorus or the oxidation of sodium sulphite (compare Bredig and Ikeda, this vol., ii, 441).

L. M. J.

Absorption of Water Vapour by definite Chemical Compounds; Distribution of the Absorbed Water between two Similar and two Dissimilar Substances. By W. I. BUSNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 412—427. Compare Abstr., 1899, ii, 360, 409, and this vol., ii, 58).—The author has extended his observations to the cases of (1) three different quantities of sulphuric acid of the same concentration placed under the same bell jar in presence of water, and (2) of three and (3) four quantities of aqueous sulphuric acid of different concentrations placed under the same bell jar. Certain relations are drawn between the rate at which water is lost or gained by the various solutions and the number of molecules of water they contain.

T. H. P.

Influence of Non-Electrolytes on the Hydrolysis of Ethyl Acetate. By CARL KULLGREN (*Zeit. physikal. Chem.*, 1901, 37, 613—622).—The influence of various compounds on the velocity of hydrolysis of ethyl acetate by sodium hydroxide solutions was investigated at the temperature of 20.7°. The compounds employed were sucrose, glycerol, methyl alcohol, ethyl alcohol, and acetone; it was found that the effect of the first two was far greater than that of the other compounds, 5 per cent. of sucrose lowering the reaction constant to the extent of 73 per cent. In this case, the results are completely explained by the supposition that sodium succinate is formed, and it is probable that in the case of glycerol also chemical action takes place. The effect of the compounds is far less marked and cannot be ascribed to chemical action; the lowering of the dissociation of the sodium hydroxide and the increase of internal friction are insufficient to account for the lowering of the velocity, which the author considered is best explained by the assumption of active and inactive molecules of ethyl acetate, the number of the latter being increased by the substitution of other compounds for water.

L. M. J.

Action of Bases and Acids on Salts of the Amines. By ALBERT COLSON (*Compt. rend.*, 1901, 132, 1563—1565. Compare Abstr., 1897, ii, 314).—An interaction between dry ammonia gas and piperidine hydrochloride takes place at 0° when the pressure is 1255 mm., and the organic base is liberated. If the pressure is subsequently lowered, the reaction is not completely reversed because of the formation of compounds of the type $\text{NH}_4\text{Cl}_n\text{NH}_3$; on the other

hand, the inverse change is brought about by adding 1 mol. of piperidine to 1 mol. of ammonium hydrochloride; the action is instantaneous, and the pressure produced is practically equal to that required for the direct decomposition. The interaction does not take place at the ordinary temperature when the substances are perfectly dry, but an action sets in at 100° or on introducing a trace of water. The hydrochlorides of diisobutylamine and piperidine absorb hydrogen chloride, giving rise to products which are liquid at 20°. The vapour pressure of diisobutylamine dihydrochloride at 34° is only 760 mm.

This property of absorbing hydrogen chloride seems to depend on chemical constitution rather than on the avidity of the base. Ammonia is intermediate in strength between diisobutylamine and piperidine, but its hydrochloride does not absorb hydrogen chloride, even at -21° and under a pressure of 3154 mm. G. T. M.

Racemisation. By JULES MINGUIN and E. GRÉGOIRE DE BOLLE-MONT (*Compt. rend.*, 1901, 132, 1573—1576. Compare Kipping and Pope, *Trans.*, 1897, 51, 989; 1899, 55, 36).—The racemic modifications of benzylidenecamphor, bornyl succinate, chloral campholate, bromal campholate, and benzylbromocamphor crystallise in forms differing from those of their active components; the active and racemic modifications of benzylidenebromocamphor and anisylidenecamphor are crystallographically identical. These racemic compounds with the exception of *r*-benzylbromocamphor are more soluble than their active components, and have lower melting points and sp. gravities. In every case, the determination of the molecular weight by the cryoscopic method indicates that the racemic compounds have simple molecular weights. When the racemic and active modifications differ in crystalline form, it is found that a mixture of the two substances in equal proportions melts at a temperature lower than the melting point of the more fusible component; when the active and inactive substances are isomorphous, the mixture melts at a temperature intermediate between the melting points of its constituents. This difference serves to distinguish between racemic and pseudoracemic compounds, benzylidenebromocamphor and anisylidenecamphor belonging to the latter category, whilst the other inactive substances enumerated are truly racemic. G. T. M.

Invariant Theory for Chemists. By E. STUDY (*Zeit. physikal Chem.*, 1901, 37, 546—550).—A criticism of the utility of the invariant theory of Gordan and Alexéeff (this vol., ii, 13). L. M. J.

Relations between Atomic Weight, Atomic Volume, and Melting Point. By THOMAS BAYLEY (*Chem. News*, 1901, 83, 243—245. Compare *Abstr.*, 1900, i, 369; ii, 188).—An exhaustive table is published exhibiting a connection between the atomic volume and the absolute melting point of various pairs of elements, and the "critical points" previously (*Chem. News*, 1887, 78, 157) defined by the author. J. C. P.

Titration of Acids and Alkalis of Complex Function. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 1377—1382).—An examination, by titration, of the acid or alkaline functions of

certain complex acids and bases found in the human body or its secretions, namely, glycocine, leucine, *o*-, *p*-, and *m*-aminohydroxybenzoic acids, aspartic acid, hippuric acid, taurine, uric acid, and mixtures of uric acid with phosphates, using litmus, methyl-orange, phenolphthalein, and Poirrier's blue, C_4B , as indicators.

C. H. B.

Inorganic Chemistry.

New Explosive and Detonating Materials. V. By UGO ALVISI (*Gazzetta*, 1901, 31, i, 221—243. Compare Abstr., 1900, ii, 205).—The author gives calculations of the potential energy of a hypothetical mixture of potassium nitrate, ammonium nitrate, potassium chlorate, potassium perchlorate, or ammonium perchlorate with hydrogen. The results show that, leaving out potassium chlorate and perchlorate, the explosive mixtures of which with hydrogen have a potential energy comparable with that of nitroglycerol, ammonium perchlorate has the highest potential energy of the oxidising salts. Further, explosive mixtures having ammonium perchlorate as their basis are entirely resolved at the moment of explosion into gaseous products, and thus develop a far greater pressure than is possible in the case of potassium chlorate or perchlorate mixtures. The following table gives roughly the propulsive forces of various black powders:

| | |
|--|-----------|
| Ordinary black powder..... | 1 |
| Black powder with potassium chlorate | 2 (about) |
| " " " perchlorate | 2.4 (") |
| Powder of ammonium perchlorate, sulphur, and carbon. | 3. |

Ammonium chlorate would give effects surpassing those obtained with the perchlorate if it could be prepared in a stable and manageable form.

Calculations have also been made of the potential energy and volume of gas after explosion of detonating and explosive mixtures of ammonium perchlorate with picric acid, mercury fulminate, charcoal, sulphur, sulphur and carbon, cellulose, various nitrocelluloses, or with finely divided metals such as zinc and aluminium. The numbers obtained show that ammonium perchlorate mixtures compare favourably with other explosives and are to be preferred to dynamite.

The results of the author's calculations, although necessarily approximate, bear out his experimental data (*loc. cit.*). T. H. P.

Constitution of Water. By HUGO WITT (*Öfver. K. Vetensk. Akad. Förhandl.*, 1900, 57, 63—83).—The author works out more fully a theory previously advanced by de Coppet and by Röntgen as to the constitution of water. According to this theory, water consists mainly of double molecules, $(\text{H}_2\text{O})_2$, and more complex molecules, $(\text{H}_2\text{O})_n$, "ice molecules," whilst the number of simple molecules, H_2O , is small

at low temperatures. By calculations based on Ramsay and Shields' association factor for water, the author finds that the most probable value for n is 8. It is further shown that when a substance is dissolved in water, the number of double molecules increases at the expense of the "ice molecules," and on the supposition that the latter have the same specific volume as ice, the theory explains the contraction which accompanies solution. The theory also interprets satisfactorily the displacement of the temperature of maximum density in solutions, the small specific heat of aqueous solutions, the absorption of heat accompanying solution, the abnormal lowerings of the vapour pressure, and the excessive increase of osmotic pressure with the concentration (compare also van Laar, *Abstr.*, 1900, ii, 189).

J. C. P.

Density of Ozone. By ALBERT LADENBURG (*Ber.*, 1901, 34, 1834. Compare this vol., ii, 232 and 380).—The author denies the validity of Otto's claims to priority.

J. J. S.

New Mode of Formation of Wöhler's Blue (or Green) Sulphur. By N. A. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 397—399).—The action of sulphur monochloride in benzene solution on metallic sulphides, especially bismuth sulphide, yields a green powder which, when dried or when treated with alcohol, becomes yellow; it is insoluble in water or acids, melts and, when heated, burns leaving an inappreciable residue, and has all the properties of precipitated sulphur. The green powder, which is only stable when kept under benzene, the author considers to be identical with the blue modification of sulphur obtained by Wöhler by the interaction of solutions of ferric chloride and hydrogen sulphide. The author has also obtained, by means of bismuth sulphide, a green variety of sulphur which becomes perfectly white on drying and contains a small quantity of bismuth chloride; similar results are obtained with zinc and cadmium sulphides.

T. H. P.

Formation of the Green Variety of Sulphur. By N. A. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 400—403. Compare preceding abstract).—The author draws an analogy between the formation of Wöhler's blue modification of sulphur by the oxidation of hydrogen sulphide with ferric chloride and the formation of ozone by oxidising water with fluorine.

A number of experiments have been made to determine the conditions of formation of green sulphur (*loc. cit.*). Besides by the action of sulphur monochloride on metallic sulphides in benzene solution, it is formed, only in smaller quantity, by the interaction of these compounds in the absence of any solvent. The influence of various solvents has also been investigated.

The green modification of sulphur is amorphous, and is not soluble in any solvent except carbon disulphide, to which it imparts but a pale green tint. It loses its colour when dried or when acted on by water, alcohol, or ether, and can only be kept under benzene, toluene, carbon disulphide, or olive oil; when placed under commercial xylene, it rapidly

acquires a blue, and afterwards a red, tint. When it is heated with persulphuric acid, the latter assumes a yellow colour; it is oxidised by hot nitric acid.

T. H. P.

Catalytic Reactions. I. Aluminium Chloride. By OTTO RUFF (*Ber.*, 1901, 34, 1749—1758).—Sulphur crystallises unchanged from sulphuryl chloride when the two substances are heated together at 130° and subsequently allowed to cool; chlorination of the sulphur only takes place at a temperature of about 200°, but in presence of aluminium chloride the reaction $\text{SO}_2\text{Cl}_2 + 2\text{S} = \text{S}_2\text{Cl}_2 + \text{SO}_2$ takes place quantitatively at temperatures between 30° and 70°, whilst with one atom of sulphur the reaction $\text{SO}_2\text{Cl}_2 + \text{S} = \text{SCl}_2 + \text{SO}_2$ takes place quantitatively at 40°; thionyl chloride is not produced under these conditions. Cinnabar does not react with sulphuryl chloride alone, but in presence of aluminium chloride is converted into mercuric chloride, which is slightly soluble in the sulphuryl chloride. The two sulphides of antimony and of tin dissolve as chlorides in sulphuryl chloride with separation of sulphur, but in presence of aluminium chloride sulphur dichloride is produced.

Sulphuryl chloride does not interact with iodine alone, but in presence of aluminium chloride or iodide the compounds ICl and ICl_3 are produced, the latter being only formed when the sulphuryl chloride is in considerable excess.

Molybdenum pentachloride readily dissolves in sulphuryl chloride to a brown solution, and is then readily reduced (by sulphur, for example) to the yellow dichloride; on adding aluminium chloride, it is immediately rechlorinated with evolution of sulphur dioxide, and, on cooling, a double-compound of molybdenum pentachloride and sulphur chloride separates from the solution.

Thionyl chloride is indifferent towards sulphur even in presence of aluminium chloride, and this behaviour can be used in order to separate it from sulphuryl chloride; the reaction $2\text{SOCl}_2 + 2\text{H}_2\text{S} = 4\text{HCl} + \text{SO}_2 + 3\text{S}$ takes place very much more vigorously when aluminium chloride is also present.

Sulphur crystallises unchanged from a solution of phosphorus pentachloride in oxychloride, but is converted into monochloride if aluminium chloride is added to the mixture.

In presence of aluminium chloride, arsenic interacts with hydrogen sulphide to form arsenious sulphide and hydrogen chloride, and also with phosphorus to form a red compound, insoluble in arsenic chloride and containing aluminium chloride; when this compound is decomposed by water, it gives a violet-black substance of the composition PAs_4O_2 (compare Janowsky's $\text{P}_2\text{As}_3\text{O}_2$, *Abstr.*, 1876, i, 681). Antimony trichloride also interacts with phosphorus in presence of aluminium chloride.

By the action of sulphur dichloride on a solution of aluminium chloride in sulphuryl chloride, a double chloride, $\text{AlCl}_3\cdot\text{SCl}_2$, is produced; it crystallises in needles, is immediately decomposed by water, and, when heated, begins to give off chlorine at 25°, loses sulphur monochloride above 65°, and finally leaves behind a hard mass of aluminium chloride.

T. M. L.

Potassium Perselenate. By LOUIS M. DENNIS and OLIVER W. BROWN (*J. Amer. Chem. Soc.*, 1901, **23**, 358—359).—*Potassium perselenate* is obtained by the electrolysis of a saturated solution of potassium selenate containing a little free selenic acid; platinum electrodes are employed, and the temperature is kept at 4°. The salt has not been obtained free from the selenate, the highest percentage of perselenate in the product being 74.44. Potassium perselenate, when hot, converts manganese dioxide into potassium permanganate, and rapidly oxidises ferrous and thalious sulphates in the cold. When an aqueous solution of the salt is warmed, oxygen is evolved.

E. G.

Tellurium. By ALEXANDER GUTBIER (*Ber.*, 1901, **34**, 2114—2115).—The determination of the mol. weight of telluric acid by the cryoscopic method indicates that the substance has the formula H_6TeO_6 , and not $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$; moreover, the acid crystallises in the hexagonal (rhombohedral) system, and not in monoclinic forms. Telluric acid is only feebly acidic, and electrical conductivity determinations show that its strength is comparable with that of hydrogen sulphide or prussic acid; it does not yield esters, and can be titrated by means of indicators. Tellurous and telluric acids, and the salts in neutral, acid, or alkaline solutions, are quantitatively reduced to tellurium by means of hydrazine hydrate. Potassium tellurate crystallises with 5 or $2\text{H}_2\text{O}$, the latter modification of the salt being isomorphous with potassium osmate, $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$.

The double salt of telluric acid with silver and lead nitrates do not exist (compare Oppenheim, *J. pr. Chem.*, 1857, **71**, 270). The tellurates of the alkaline earth metals cannot be obtained crystalline. Tellurites are produced on melting tellurates. Telluric acid combines with aniline, but oxidises the aromatic diamines.

G. T. M.

Nitration by means of Nitrates in presence of Water. By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 393—397).—The author has made a number of experiments on the nitration of various hydrocarbons by heating them in sealed tubes with aqueous solutions of various nitrates. The results lead to the following conclusions. Nitrates of the alkali metals and of ammonia undergo little or no hydrolysis in presence of water at 125°; the concentration of the nitric acid formed must be less than 0.14 per cent. At the same temperature, bismuth, aluminium, mercury, and silver nitrates are considerably hydrolysed, the bismuth salt to the greatest extent. Thus the nitrates of the heavy metals and of aluminium may in some cases be advantageously employed in place of nitric acid as nitrating agents, and as no appreciable oxidation takes place, they would be especially valuable for the nitration of hydroxy-compounds. Boric acid or carbon dioxide at 100°, or silica at a low red heat, do not displace nitric acid to any appreciable extent from its salts. Boric acid and carbon dioxide do, however, liberate nitrous acid from nitrites, whilst oxalic and sulphuric acids set free both nitrous and nitric acids from their salts.

T. H. P.

Preparation of Phosphorus Sub-oxide. By ADOLPHE BESSON (*Compt. rend.*, 1901, 132, 1556—1557. Compare Abstr., 1898, ii, 216; 1900, ii, 539, and Michaelis and Pitsch, Abstr., 1895, ii, 285; 1900, ii, 137).—The author has again estimated the phosphorus in the oxide prepared by the action of phosphine on a cold, saturated solution of hydrogen bromide in phosphorus oxychloride, and finds that the numbers point to the formula P_2O rather than to P_4O . This oxide is also produced by oxidising phosphorus dissolved in warm phosgene with a current of dry air, and by the action of phosphorous acid on phosphorus trichloride at 100° .
G. T. M.

Neutralisation of Phosphoric Acid. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 1277—1281. Compare Abstr., 1887, 94).—When a dilute solution of calcium hydroxide is slowly added to a dilute solution of phosphoric acid, the point of neutralisation, as indicated by methyl-orange, is attained when the acid and basic oxide are in the proportion $2H_3PO_4, CaO$. If a further quantity of the alkaline solution is quickly added to the mixture, a precipitate of $CaHPO_4$ is produced, the deposition being complete when the acid and alkali are present in mol. proportion. In the presence of excess of the alkali, the precipitate gradually alters in composition, taking up excess of calcium oxide, 1 mol. of the acid fixing 4 and even 10 CaO . When the titration is made by slowly adding the acid to the alkali, the neutral point, as indicated by methyl-orange, is reached when these reagents are in the proportion corresponding with $P_2O_5, 2CaO$; with phenolphthalein, the end-point is less definite and corresponds with 1.4 CaO . The precipitate obtained by adding excess of lime water to a solution of phosphoric acid has approximately the composition of a tetrabasic phosphate. When shaken up with water, this substance forms an emulsion which is clarified very slowly. The deposition is, however, greatly accelerated either by the addition of a saturated solution of sodium chloride, or by maintaining the mixture for 6 hours at 60° , the coagulate obtained having a composition corresponding with $H_3PO_4, 2CaO$.

When phosphoric acid is titrated with baryta water, the neutralisation point corresponds with the formation of the salt $BaO, P_2O_5, 2H_2O$, the inverse operation giving an end-point when the salt $BaHPO_4$ is precipitated.

The insoluble barium and calcium phosphates produced by double decomposition vary in composition according to the constitution of the original soluble alkali phosphate, and the amount of this reagent employed. Barium salts of the following type, $BaHPO_4, 3BaO, P_2O_5$ and $2NaOH, 2BaO, P_2O_5$, have been obtained, together with others intermediate in composition; similar compounds are known containing calcium.
G. T. M.

Acidimetry of-Phosphoric Acid with the Hydroxides of Calcium, Strontium, and Barium. By JACQUES CAVALIER (*Compt. rend.*, 1901, 132, 1330—1331. Compare preceding abstract).—The replacement of one of three hydrogen atoms of phosphoric acid by barium is readily indicated either by methyl-orange or *p*-nitrophenol, especially when dilute solutions of the acid and barium hydroxide are employed.

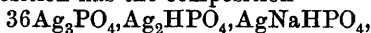
When the concentration is too great, a gelatinous precipitate of $\text{Ba}_3(\text{PO}_4)_2$ is formed, and the end point becomes uncertain. The replacement of the second hydrogen atom by further addition of barium hydroxide is clearly indicated by phenolphthalein, provided that sufficient time is allowed to permit of the gelatinous tribarium phosphate being converted into the crystalline dibarium salt; this result is attained either with dilute or concentrated solutions; in the latter case, however, it is preferable to warm the mixture in order to accelerate the production of the crystalline precipitate. Concentrated solutions of strontium hydroxide produce similar results, but in dilute solutions the formation of the crystallised distrontium salt requires several hours, and a sharp end point is obtained only in the cold. Calcium hydroxide cannot be conveniently employed instead of its barium analogue, because the crystalline salt, CaHPO_4 , is only produced with certainty when the solutions are not too dilute and when the addition of the alkali is carried out very slowly and in the cold. In dilute solutions, an end point with phenolphthalein is obtained when sufficient calcium hydroxide has been added to completely saturate the phosphoric acid; this titration is not, however, very accurate. G. T. M.

Formation of Insoluble Phosphates by Double Decomposition: Disodium Phosphate and Silver Nitrate. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 1449—1459. Compare preceding abstracts).—When solutions containing silver nitrate and sodium phosphate in mol. proportions are mixed at the ordinary temperature, the silver is completely precipitated; the deposit, even after repeated washing, contains small amounts of sodium and hydrogen, and has a composition corresponding with $18\text{Ag}_3\text{PO}_4 \cdot \text{Ag}_2\text{HPO}_4 \cdot \text{NaAgHPO}_4$. The filtrate is acid to phenolphthalein and alkaline to methyl-orange, requiring $\frac{1}{3}\text{NaOH}$ to produce neutrality in the first case and $\frac{1}{3}\text{HCl}$ to bring about a similar result in the second. The liquid is also alkaline to litmus, but with this indicator the end point is indefinite. Leaving out of account the presence of alkali salt in the precipitate, the foregoing double decomposition may be approximately represented by the following equation: $3\text{AgNO}_3 + 3\text{Na}_2\text{HPO}_4 = \text{Ag}_3\text{PO}_4 + \text{Na}_2\text{HPO}_4 + \text{NaH}_2\text{PO}_4 + 3\text{NaNO}_3$. The end points obtained with phenolphthalein and methyl-orange correspond with the total conversion of the soluble phosphate into disodium and monosodium salts respectively.

When the reaction is effected on the water-bath, the precipitate contains far less sodium, although this element is still present in appreciable quantity.

When 2 mols. of silver nitrate react in the cold with 1 mol. of disodium phosphate, the precipitation of the triargentic salt is not complete, the amount deposited corresponding with $0.543 \text{ Ag}_3\text{PO}_4$. The filtrate is acid both to methyl-orange and phenolphthalein, the end points being attained by the addition of $\frac{1}{3}$ and $\frac{2}{3}$ mol. of sodium hydroxide respectively. The remainder of the silver is precipitated as the liquid becomes neutral to phenolphthalein. The double decomposition may be approximately represented as follows: $2\text{AgNO}_3 + \text{Na}_2\text{HPO}_4 = 2\text{NaNO}_3 + 0.543 \text{ Ag}_3\text{PO}_4 + 0.37 \text{ AgH}_2\text{PO}_4(\text{sol.}) + 0.087 \text{ H}_3\text{PO}_4$. This equation, however, assumes that all the nitric

acid is neutralised, whereas a portion probably exists in the free state, equilibrium being established between the two acids in presence of the two basic oxides of sodium and silver. The precipitate obtained in the double decomposition has the composition



whereas that produced by the subsequent addition of sodium hydroxide corresponds with the formula $13\text{Ag}_3\text{PO}_4, \text{Ag}_2\text{HPO}_4, \text{AgNaHPO}_4$.

The solution obtained when 3 mols. of silver nitrate react with 1 mol. of disodium phosphate is acid to both methyl-orange and phenolphthalein, and in this case the amounts of sodium hydroxide required to produce neutrality are the same, namely, 1 mol. The addition of the alkali produces a second precipitate of triargentate phosphate. The course of the initial reaction may be approximately represented by the equation $3\text{AgNO}_3 + \text{Na}_2\text{HPO}_4 = 2\text{NaNO}_3 + 0.779\text{AgNO}_3 + 0.221\text{HNO}_3 + 0.603\text{Ag}_3\text{PO}_4 + 0.397\text{AgH}_2\text{PO}_4$. The precipitates obtained in this case contain only traces of sodium, and correspond in composition with the triargentate salt.

These results indicate that on mixing solutions of silver nitrate and disodium phosphate in the cold, the silver is completely precipitated when the salts react in mol. proportions, whereas the total precipitation of phosphoric acid occurs only on adding 1 mol. of sodium hydroxide to a solution which contains the reagents in the proportion $1\text{Na}_2\text{HPO}_4 : 3\text{AgNO}_3$.

G. T. M.

Reactions of Two Basic Oxides exposed simultaneously to the Action of Phosphoric Acid. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 1517—1525. Compare preceding abstract).—The filtrate from the mixture produced by mixing together solutions of phosphoric acid, sodium, and calcium hydroxides in the following proportions ($2\text{H}_3\text{PO}_4 : 4\text{NaOH} : \text{CaO}$) is alkaline both to methyl-orange and phenolphthalein, and it follows that the solution must contain soluble tribasic phosphates R_3PO_4 . The amounts of soluble di- and tri-basic salts are estimated by titrations with the two indicators, methyl-orange being neutral to monobasic phosphates and phenolphthalein to the dibasic compounds. The quantity of phosphoric acid (2 mols.) remaining dissolved is only 0.74 mol., whilst the precipitate contains at least 2 mols. of sodium hydroxide to 1 mol. of calcium oxide, the composition of the insoluble phosphate agreeing approximately with the formula $\text{Ca}_3(\text{PO}_4)_2, 2\text{Na}_3\text{PO}_4$. This composition is, however, based on the hypothesis that all the calcium is precipitated, an assumption which is practically correct after 48 hours. When the alkaline mixture consists of barium and sodium hydroxides in the ratio $\text{BaO} : 4\text{NaOH} : 2\text{H}_3\text{PO}_4$, a similar result is obtained, the insoluble phosphate containing at least 50 per cent. of the sodium; a further increase in the amount of sodium phosphate carried down is noticed when the precipitate is left in contact with the mother liquor.

The alkalis, when added to the acid in the proportions necessary to form dibasic salts ($2\text{H}_3\text{PO}_4, \text{CaO}, 2\text{NaOH}$) or ($2\text{H}_3\text{PO}_4, \text{BaO}, 2\text{NaOH}$) yield solutions which are alkaline to both indicators. In the case of the mixture containing calcium, the composition of the insoluble phosphate varies with the time. Immediately after mixing, the phosphoric

acid is divided between solution and precipitate in accordance with the following ratio : $0.48\text{R}_2\text{HPO}_4$, $0.25\text{RH}_2\text{PO}_4$ (sol. salts), $1.27\text{H}_3\text{PO}_4$ (as insoluble di- and tri-basic phosphates). After prolonged contact of the precipitate and solution, the following numbers : $0.39\text{R}_2\text{HPO}_4$, $0.29\text{RH}_2\text{PO}_4$ (soluble salts), $1.32\text{H}_3\text{PO}_4$ (as insoluble di- and tri-basic phosphates) indicate the condition of the phosphoric acid. When barium hydroxide is employed, the composition of the insoluble product is the same whether it is separated immediately or left in contact with the solution, the ratio in this case being thus indicated : $0.52\text{R}_2\text{HPO}_4$, $0.05\text{RH}_2\text{PO}_4$ (soluble salts), $1.43\text{H}_3\text{PO}_4$ (as insoluble di- and tri-basic phosphates).

These results indicate that when these mixtures of basic oxides are employed to neutralise phosphoric acid, the quantity of acid precipitated is greatly in excess of that corresponding with the calcium or barium oxide present ; in every case examined, the precipitate contains a considerable amount of sodium phosphate.

G. T. M.

Action of Cuprous Salts on Carbon Monoxide. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1901, [v], 23, 32—39).—See this vol., i, 493.

Repelling of the Ionisation of Solutions of Sodium Hydroxide, Carbonate, and Hydrogen Carbonate by Addition of Sodium Chloride. By A. SMITS and L. K. WOLFF (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 42—44).—Starke (this vol., i, 242) found that (1) addition of dilute sodium hydroxide to a 15 per cent. sodium chloride solution gave a more alkaline solution than when it was added to water. (2) With sodium carbonate and sodium hydrogen carbonate, the result was the same. He also stated (3) that sodium chloride cannot be precipitated from its strong solution by concentrated sodium hydroxide solution.

These experiments have been repeated, and the results (1 and 2) are confirmed provided that the solvent water contains carbon dioxide. If the water is free from carbon dioxide, then the ionisation of the sodium hydroxide is diminished by the addition of sodium chloride and, as theory requires, the alkalinity is decreased. Starke's result is explained by some of the dissolved carbon dioxide being expelled by the sodium chloride ; the water before solution of the chloride had, therefore, a stronger acid reaction, and this was so predominant as to exceed the decrease of ionisation of the alkali caused by the sodium chloride. Starke's observation that sodium chloride cannot be precipitated by sodium hydroxide has been experimentally disproved.

J. McC.

Demonstration of the Action of Normal Salts on Solutions containing Hydroxyl Ions. By G. DOYER VAN CLEEFF (*Rec. Trav. Chim.*, 1901, 20, 198—205).—Ammonium salts added to solutions containing hydroxyl ions diminish the concentration of these by the formation of ammonium hydroxide which is only slightly dissociated. This is shown by various reactions with indicators. Ammonium salts convert manganates and chromates into permanganates and dichromates in dilute solutions. Manganese borate, magnesium hydr-

oxide, and litharge are more soluble in ammonium salt solutions than in pure water.

That the addition of potassium or sodium chloride also diminishes the concentration of hydroxyl ions is shown (1) by solutions of potassium silicate to which these salts have been added becoming opalescent whilst pure aqueous solutions remain clear; (2) by the conversion of manganate in slightly alkaline solution into permanganate, and (3) by some reactions with indicators.

Hydroxylamine hydroxide being little dissociated in solution, the addition of its hydrochloride also causes a diminution of the concentration of the hydroxyl ions, as may be proved by its turning colourless a lightly alkaline solution containing phenolphthalein.

J. McC.

Action of Solar Radiations on Silver Chloride in the Presence of Hydrogen. By JOUNIAUX (*Compt. rend.*, 1901, 132, 1558—1560. Compare Abstr., 1900, ii, 139).—When silver chloride surrounded by an atmosphere of hydrogen is exposed to the action of the sun's rays, the chloride is reduced and hydrogen chloride is produced. When suitable amounts of the silver salt are employed and the exposure is continued for 18 months, practically the whole of the hydrogen is transformed into hydrogen chloride; the velocity of reaction depends, however, very largely on the state of aggregation of the solid reagent. At the ordinary temperature, this mixture of silver salt and hydrogen is in stable equilibrium as long as it is kept in the dark, as under these conditions the reaction only sets in at about 250°.

G. T. M.

Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XXII. Gypsum and Anhydrite. II. The Soluble Anhydrite (CaSO_4). By JACOBUS H. VAN'T HOFF, WILLY HINRICHSSEN, and FRITZ WEIGERT (*Sitzungsber. K. Preuss. Akad. Wiss.*, 1901, 570—578. Compare van't Hoff and Armstrong, Abstr., 1900, ii, 531).—By dehydration of gypsum at low temperatures, an anhydrous calcium sulphate is obtained which is fairly easily soluble and sets with great rapidity; thus there are two modifications of anhydrite. The temperature of transformation of gypsum into anhydrite is, contrary to what might be expected, below 107° (*loc. cit.*). This has been confirmed by a number of comparative vapour tension determinations, and a formula is deduced for the vapour tension of the system gypsum-anhydrite, showing its variation with the temperature. A small extrapolation of this formula gives 89° as the temperature of transformation of gypsum into anhydrite. At that temperature, therefore, the hydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, is metastable.

J. C. P.

Simultaneous presence of Barium and Sulphates in Mineral Waters. By P. CARLES (*J. Pharm.*, [vi], 13, 562—565).—In order to account for the simultaneous presence of barium and alkali sulphates in the mineral water of Nérès-les-Bains, the following experiment was made. A specimen of the barytes of the district (containing silicofluoride) was boiled with twice its weight of sodium carbonate until partly converted into barium carbonate. The still alkaline paste was

then supersaturated with carbon dioxide under pressure and filtered after 12 hours. The perfectly clear filtrate, which contained sodium sulphate, deposited barium carbonate (together with strontium and calcium carbonates) when the excess of carbon dioxide was expelled by heating. It is therefore evident that alkali hydrogen carbonates in presence of an excess of carbon dioxide, are capable of holding barium hydrogen carbonate in solution in the presence of soluble sulphates. The presence of lead in the same mineral water is most likely capable of a similar explanation.

M. J. S.

Barium Nitrite. By KURT ARNDT (*Zeit. anorg. Chem.*, 1901, 27, 341—358).—A pure barium nitrite cannot be prepared from the commercial product which contains nitrate, as it is impossible to separate the nitrite and nitrate either by crystallisation from water or alcohol, or by fractional precipitation of the aqueous solution with alcohol. The usual methods of formation, namely, by heating barium nitrate, by saturating barium hydroxide with nitrous acid, and by reducing the nitrate with lead sponge, also yield an impure nitrite which cannot be purified. The pure nitrite is obtained by shaking silver nitrite, mixed with washed sand and water, with barium chloride and evaporating the filtrate on the water-bath. When the aqueous solution is crystallised at the ordinary temperature over sulphuric acid, it has the composition $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$; when crystallised at a higher temperature, it contains rather less water. It is soluble in its own weight of water, gives a colourless solution which is neutral to litmus, and when dried is slightly decomposed with the formation of barium hydroxide. It melts at about 220° . Even after prolonged ignition, decomposition is not complete, the mass still containing a small quantity of nitrite.

E. C. R.

Cadmium Amalgams. By HENDRIK W. BAKHUIS ROOZEBOOM [and BYL] (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 1—5).—None of the liquid amalgams of cadmium solidifies completely at a constant temperature. Amalgams containing less than 67 per cent. of cadmium solidify to homogeneous mixed crystals of the mercury type, and those containing more than 77 per cent. solidify to homogeneous mixed crystals of the cadmium type. It is shown that for the Weston cell to have a constant *E.M.F.* it is necessary for the amalgam forming the negative pole to contain rather more than 70 per cent. of cadmium.

R. H. P.

Thallium Chlorobromides. By VICTOR THOMAS (*Compt. rend.*, 1901, 132, 1487—1489. Compare this vol., ii, 60, 100, 159).—Bromine reacting with thallous chloride in the presence of neutral solvents, chloroform, or carbon tetrachloride, yields the chlorobromide, $\text{Tl}_3\text{Cl}_2\text{Br}_4$. When the solvent is capable of combining with the halogens, the chloride is transformed into the dibromide, TlBr_2 ; this transformation is complete when sufficient excess of bromine is employed dissolved in carbon disulphide. The additive product, TlClBr , is produced when bromine vapour is passed over thallous chloride, a similar result being obtained on gently heating the reagents in sealed tubes.

G. T. M.

Results of Chilling Copper-Tin Alloys. By CHARLES T. HEYCOCK and FRANCIS H. NEVILLE (*Proc. Roy. Soc.*, 1901, 68, 171—178).—The results of a microscopical study of copper-tin alloys, and a discussion of the light thus thrown on the changes which take place when the alloys cool. The cooling curve for an alloy with 19 atomic per cents. of tin was first obtained, and the points determined at which development of heat took place. On the basis of this curve, certain temperatures were selected at which the cooling alloy was suddenly chilled by immersion in water. In order to bring out the pattern, the chilled alloys, after being ground and polished, were slightly heated until the film of oxide formed was of a pale yellow colour. It seems that for alloys richer in copper than Cu_3Sn , the parts which oxidise most rapidly and are therefore darkest in the yellow stage are the softer parts containing most copper. It is hardly possible to describe the observations made without the aid of the accompanying photographs. The authors find that the patterns of slowly-cooled copper-tin alloys are, until they have been confirmed by the examination of chilled portions, entirely misleading as to the separations which occur during solidification. The evidence for the existence of the compound Cu_3Sn will have to be revised.

J. C. P.

Commercial Copper Oxide. By PAUL DRAWE (*Zeit. angew. Chem.*, 1901, 14, 586—587).—Commercial copper oxide as used in glass factories often contains appreciable amounts of cuprous oxide, which interferes with the development of the required colour. The percentages of cuprous and cupric oxides present are determined by treatment with dilute sulphuric acid; the metallic copper which is deposited is removed, heated in a stream of hydrogen, and then dissolved in nitric acid, and the copper estimated by any of the ordinary methods. The copper sulphate in the filtrate from the finely divided metal is estimated by the aid of potassium thiocyanate.

J. J. S.

Action of a Metallic Hydroxide on Solutions of Salts of other Metals; Basic Salts of Two Metals. By ALBERT RECOURA (*Compt. rend.*, 1901, 132, 1414—1416).—The author has investigated the action of freshly prepared cupric hydroxide on solutions of certain metallic sulphates at the ordinary temperature and when hot, and has obtained the following products:

Zinc sulphate, when hot, a pale bluish-green compound, $\text{ZnSO}_4 \cdot 3\text{CuO}$; when cold, a pale blue compound, $7\text{ZnSO}_4 \cdot 24\text{CuO}$.

Cadmium sulphate, when hot, a pale blue compound, $\text{CdSO}_4 \cdot 3\text{CuO}$; when cold, a bright blue compound, $6\text{CdSO}_4 \cdot 20\text{CuO}$.

Manganous sulphate, when hot, a grey-green compound, $\text{MnSO}_4 \cdot 3\text{CuO}$; when cold, a green compound, $\text{MnSO}_4 \cdot 24\text{CuO}$.

Cobalt sulphate, when hot, a pale greenish compound, $\text{CoSO}_4 \cdot 3\text{CuO}$; when cold, a blue compound, $\text{CoSO}_4 \cdot 24\text{CuO}$.

Nickel sulphate, when hot, a pale greenish-blue compound, $5\text{NiSO}_4 \cdot 16\text{CuO}$; when cold, a bright blue compound, $\text{NiSO}_4 \cdot 20\text{CuO}$.

Cupric sulphate, whether hot or cold, a pale green compound, $\text{CuSO}_4 \cdot 3\text{CuO}$.

Except in the case of nickel, the products formed in the hot solutions are all of the same type, but those formed at the ordinary temperature vary considerably in type. C. H. B.

Action of a Metallic Oxide or Hydroxide on Solutions of Salts of other Metallic Radicles. By PAUL SABATIER (*Compt. rend.*, 1901, 132, 1538—1540. Compare preceding abstract).—The author calls attention to his previous communications on this subject, and classifies the different modes of action between the metallic oxides or hydroxides and the salts of other metals dissolved in water (compare Abstr., 1897, ii, 26, 491, 553; 1899, ii, 654). G. T. M.

Action of Mercuric Oxide on Aqueous Solutions of Metallic Salts. By A. MAILHE (*Compt. rend.*, 1901, 132, 1560—1563. Compare Sabatier, preceding abstract).—With manganous chloride solution, recently precipitated mercuric oxide yields a precipitate of manganous hydroxide, which rapidly darkens owing to oxidation, the final product being a mixture of manganese oxychloride and manganic oxide. Mercuric oxide has no action on the sulphate, even after several months; with the nitrate, it yields white, crystalline, hexagonal prisms having the composition $\text{Hg}(\text{NO}_3)_2 \cdot \text{MnO} \cdot 3\text{H}_2\text{O}$; both varieties of mercuric oxide produce this result. The cadmium salts react similarly with mercuric oxide, the chloride giving an insoluble oxy-salt, $\text{CdCl}_2 \cdot \text{CdO} \cdot 7\text{H}_2\text{O}$, the nitrate yielding a crystalline basic double nitrate, $\text{Hg}(\text{NO}_3)_2 \cdot \text{CdO} \cdot 3\text{H}_2\text{O}$, whilst the sulphate remains unchanged. Lead chloride and mercuric oxide interact, forming the basic chloride, $\text{HgCl}_2 \cdot 2\text{PbO} \cdot 2\text{H}_2\text{O}$; lead nitrate, however, is not affected by the oxide.

When mercuric oxide is added rapidly to a solution of ferrous chloride from which the air is excluded, a brown precipitate is formed consisting of a mixture of mercurous chloride and basic ferric chloride; when the addition is carried out more slowly, the deposit consists entirely of the mercurous salt. The final result of the action of the oxide on a solution of ferrous sulphate is a yellow precipitate, consisting of a mixture of metallic mercury, mercurous sulphate, and basic ferric sulphate. Addition of mercuric oxide to ferric chloride solution yields an insoluble basic ferric chloride; in the case of the sulphate, a yellow powder is thrown down, having the composition of turpeth mineral; the nitrate yields the basic salt, $\text{Hg}(\text{NO}_3)_2 \cdot \text{HgO} \cdot \text{H}_2\text{O}$. G. T. M.

Basic Salts containing several Metallic Oxides. By GUSTAVE ANDRÉ (*Compt. rend.*, 1901, 132, 1563. Compare preceding abstract).—In consequence of the communications on basic double salts recently put forward by Mailhe and Recoura, the author calls attention to his earlier researches on analogous compounds (Abstr., 1887, 446, 447; 1888, 651). G. T. M.

Modifications of Mercuric Iodide. By D. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 384—387).—The temperature at which red mercuric iodide is converted into the yellow modification has been found by Gernez (Abstr., 1900, ii, 141) to be 126° . It is, however, observed that the yellow variety sometimes remains for a long time at the ordinary temperature without change, whilst the red form keeps its colour at temperatures at which transformation is possible. The

colour of solutions of mercuric iodide in organic solvents is yellow, and the yellow form is also deposited from these solutions, the colour only changing to red after some time. It would hence appear that in solution the iodide exists in the same form as it does in the state of vapour, namely, the yellow orthorhombic modification, and that the transformation temperature is considerably lowered by solvents. When potassium iodide and a mercuric salt are mixed in solution, the precipitate is at first yellow, and it is hence probable that when a double salt of mercuric iodide is decomposed by water, the yellow variety is first precipitated but is converted into the red form so rapidly as to escape observation. On cooling red mercuric iodide by means of solid carbon dioxide, a gradual but complete transformation into the yellow modification takes place. The reason of this change is not clear, since the transformation of the yellow into the red variety of the iodide is accompanied by a development of 3.0 Cal. T. H. P.

Double Salts of Mercuric Iodide with the Iodides of Nickel and Cobalt. By D. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 303—309).—The compound, $\text{NiI}_2 \cdot 2\text{HgI}_2 \cdot 6\text{H}_2\text{O}$, is obtained in the form of dirty green, prismatic, hygroscopic prisms, which are decomposed, by water or by grinding, into dirty grayish-green, drusy, crystalline masses having the composition $\text{NiI}_2 \cdot \text{HgI}_2 \cdot 6\text{H}_2\text{O}$; the latter salt, which is soluble in alcohol, ether, or acetone, is not decomposed by water, and on warming mercuric iodide is evolved.

The salt $\text{CoI}_2 \cdot 2\text{HgI}_2 \cdot 6\text{H}_2\text{O}$, has also been prepared, and forms dirty red, regular octahedra, which are soluble in alcohol or acetone, and are decomposed by the action of water or by grinding, yielding crystals of the composition $\text{CoI}_2 \cdot \text{HgI}_2 \cdot 6\text{H}_2\text{O}$, which are not attacked by water.

T. H. P.

Types of Double Salts of Mercuric Iodide with Iodides of Metals of different Valencies. By D. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 387—392).—All the double salts of mercuric iodide, with other metallic iodides investigated up to the present, may be regarded as derived from one or other of the acids having the formulæ HHgI_3 and H_2HgI_4 . The salts of the former acid are decomposed by water, half of the mercuric iodide they contain being precipitated, and the corresponding salt of the acid H_2HgI_4 formed (compare preceding abstract). It has also been found that hot concentrated hydriodic acid dissolves mercuric iodide, giving a solution of the composition HHgI_3 , and this, when sufficiently diluted with water, deposits HgI_2 , leaving in solution the acid H_2HgI_4 ; the compound HHgI_3 , which separates from solution in yellow needles, also decomposes in this way on standing in the air. No compounds of mercuric iodide with iodides of trivalent metals are as yet known. T. H. P.

Double Nitrates of Quadrivalent Cerium and of Thorium. By RICHARD JOS. MEYER and RICHARD JACOBY (*Zeit. anorg. Chem.*, 1901, 27, 359—389. Compare Abstr., 1900, ii, 597).—Basic ceric nitrate, $\text{Ce}(\text{NO}_3)_3 \cdot \text{OH} \cdot 3\text{H}_2\text{O}$, crystallises from solutions containing calcium nitrate in beautiful, red needles; when dissolved in water, it yields an acid, yellow solution, which gradually undergoes hydrolysis

and becomes almost colourless, the colour being regenerated on the addition of nitric acid; this hydrolysis takes place quickly when the solution is heated. A freshly prepared solution of the salt is at once reduced by hydrogen peroxide with evolution of oxygen, but a hydrolysed solution is at first coloured dark red owing to the formation of higher oxidation products, and then is gradually reduced.

The double nitrates of the formula $R'_2\text{Ce}(\text{NO}_3)_6$ are well crystallised, red salts, similar in appearance to the dichromates; they are very hygroscopic, show the same phenomena as ceric nitrate in aqueous solution, and are best prepared in the presence of nitric acid. The following salts are described. The ammonium salt, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, crystallises in the monoclinic system [$a:b:c=2.4668:1:2.3901$; $\beta=129^\circ 52'$]. The *potassium*, *rubidium*, and *cæsium* salts are also described, and crystallise without water. The *magnesium*, *zinc*, *nickel*, *cobalt*, and *manganese* salts crystallise with $8\text{H}_2\text{O}$, are very easily oxidised, must be prepared in the presence of strong nitric acid, crystallise in dark red or brown crystals, are decomposed when dissolved in water, and do not lose their water of crystallisation when dried over sulphuric acid.

Double nitrates of thorium nitrate. The *potassium* salt, $\text{K}_2\text{Th}(\text{NO}_3)_6$, crystallises from solution in dilute nitric acid at 80° in long prisms, and is hygroscopic. The salt $\text{KTh}(\text{NO}_3)_5 \cdot 9\text{H}_2\text{O}$ crystallises from neutral or faintly acid solutions when evaporated over sulphuric acid or potassium hydroxide, in thin, lustrous leaflets, is hygroscopic, and effloresces in the desiccator. The salt $\text{H}_3\text{K}_3\text{Th}(\text{NO}_3)_{10} \cdot 4\text{H}_2\text{O}$ crystallises from nitric acid of sp. gr. above 1.2 on evaporation over sulphuric acid and potassium hydroxide in large, transparent crystals, rapidly effloresces on exposure to air, and gives off all the free nitric acid and water when warmed. The *sodium* salt, $\text{NaTh}(\text{NO}_3)_5 \cdot 9\text{H}_2\text{O}$, resembles the potassium salt. The *ammonium* salt, $\text{NH}_4\text{Th}(\text{NO}_3)_5 \cdot 5\text{H}_2\text{O}$, is obtained from solutions of nitric acid up to sp. gr. 1.25; the salt, $(\text{NH}_4)_2\text{Th}(\text{NO}_3)_6$, from solutions in stronger acid. The isomorphous mixture, $(\text{K}, \text{NH}_4)_2\text{Th}(\text{NO}_3)_6$, is obtained by adding ammonium nitrate to a solution of the salt $\text{H}_3\text{K}_3(\text{NO}_3)_{10} \cdot 4\text{H}_2\text{O}$. The *rubidium* salt, $\text{Rb}_2\text{Th}(\text{NO}_3)_6$, and the *cæsium* salt, $\text{Cs}_2\text{Th}(\text{NO}_3)_6$, are also described. The *magnesium* salt, $\text{MgTh}(\text{NO}_3)_6 \cdot 8\text{H}_2\text{O}$, forms colourless, monoclinic crystals [$a:b:c=1.0251:1:0.8640$; $\beta=119^\circ 1'$], is very hygroscopic, effloresces in the desiccator, and is decomposed when heated with evolution of water and nitric acid. The *zinc* salt, with $8\text{H}_2\text{O}$, is monoclinic [$a:b=1.0437:1$; $\beta=118^\circ 36'$]. The *nickel*, *cobalt*, and *manganese* salts crystallise with $8\text{H}_2\text{O}$.
E. C. R.

Europium, a new Element. By EUGÈNE DEMARÇAY (*Compt. rend.*, 1901, 132, 1484—1486. Compare Abstr., 1900, ii, 481).—The oxide of the new element *europium*, ($\text{Eu}=151$ approx.), has been obtained so pure that it does not give any indication of the samarium spectra, and exhibits only faint traces of the strongest of the gadolinium lines. The anomalous ray referred by Crookes to the meta-element, S_8 , of the samarium group seems to be the most characteristic line of the new element's fluorescent spectrum, whilst the reversion spectrum exhibits the line Z_ζ of Lecoq de Boisbaudran.

Traces of the new oxide, mixed with calcium sulphate and rendered fluorescent in the vacuum tube, yield a brilliant spectrum, the wavelengths of lines of which have been measured and tabulated. The reversion and absorption spectra have already been described.

G. T. M.

Aluminium and Magnesium Alloys. By OCTAVE BOUDOUARD (*Compt. rend.*, 1901, 132, 1325—1327).—The determination of the melting points of mixtures of aluminium and magnesium effected by means of Le Chatelier's thermo-electric couple shows that there are two points of maximum (455° and 462°) and three of minimum solubility (356° , 445° , and 432°) in mixtures containing from 10 to 20 per cent. of aluminium. The two maxima indicate the existence of two compounds, AlMg_2 and AlMg . Starting from pure aluminium and gradually adding magnesium, it is found that the fragility of the mixture increases continuously, reaching a maximum when the metals are in equal proportions; this alloy is so friable that it may be broken between the fingers and pulverised in a porcelain mortar. As the amount of magnesium increases from this point onwards, the fragility diminishes.

G. T. M.

Aluminium Alloys. Compounds of Aluminium and Molybdenum. By LÉON GUILLET (*Compt. rend.*, 1901, 132, 1322—1325).—The author employs the method already indicated (this vol., ii, 388) in preparing alloys of aluminium and molybdenum. The alloy Al_4Mo forms lamellar crystals, and is formed together with AlMo , which separates in fibrous needles. The substance Al_7Mo is also obtained in crystalline aggregates. These crystals are all decomposed by concentrated acids, but are not attacked by boiling water. The dross which accompanies these crystalline products when treated with aqua regia yields well-defined crystals varying in composition. These substances are being investigated.

G. T. M.

Manganese Compounds. II. Manganic Acetate and Manganese Alums. By ODIN T. CHRISTENSEN (*Zeit. anorg. Chem.*, 1901, 27, 321—340; *Abstr.*, 1900, ii, 596).—Hydrated manganese peroxide is easily obtained by the action of potassium permanganate on a warm solution of manganous acetate. Hydrated manganomanganic oxide is prepared by triturating the hydrated peroxide with a warm solution of manganous chloride mixed with ammonium chloride and an excess of ammonia.

Manganic acetate is obtained by treating undried, hydrated manganomanganic oxide with acetic acid at the ordinary temperature, or by the action of potassium permanganate on manganous acetate in the presence of acetic acid. It can be recrystallised from warm acetic acid, and when treated with oxalic acid in the presence of potassium acetate gives a beautiful, red coloration which is due to the formation of a potassium manganic oxalate.

From manganic acetate, the manganese alums are easily prepared by dissolving it in sulphuric acid and then adding the alkali sulphate also dissolved in sulphuric acid, but it is necessary to cool the solution at -2 — 5° or better at -20 — 25° . Cæsium, rubidium, potassium, and ammonium manganese alums are described. They are very unstable;

the potassium and ammonium salts decompose at the ordinary temperature, and the caesium salt, which is the most stable, at 40° . The potassium and ammonium alums cannot, therefore, be obtained by Mitscherlich's method, which yields only a double sulphate of ammonium and manganese containing less than $24\text{H}_2\text{O}$. E. C. R.

New Method of preparing Ferrous Oxide. By JULES FÉRÉE (*Bull. Soc. Chim.*, 1901, [iii], 25, 615—617).—It is generally stated that an amalgam of iron is unstable, and easily decomposes into mercury and iron; this is not correct, for the decomposition depends on the conversion of the iron into ferrous oxide and does not take place in a vacuum or in an atmosphere of an inert gas. The oxide formed was analysed, and an experiment is also described in which the increase in weight of a piece of amalgam containing 35.72 per cent. of iron was found in six days to correspond with the oxidation of 96.54 per cent. of the iron; the oxide takes fire at about 350° and burns to magnetic oxide. T. M. L.

Cobalt Sulphide. By W. HERZ (*Zeit. anorg. Chem.*, 1901, 27, 390—392).—Cobalt sulphide, prepared by precipitating a solution of cobalt nitrate with ammonium sulphide and washing by decantation with water, is, when freshly prepared, soluble in dilute hydrochloric acid ($N/2$) with evolution of hydrogen sulphide. When allowed to remain exposed to the air, it is partially converted into sulphate, and when treated with dilute hydrochloric acid is partially soluble without any evolution of hydrogen sulphide; the remainder of the sulphide has, however, apparently polymerised, and is now insoluble. E. C. R.

Electrolytic Chromium. By JULES FÉRÉE (*Bull. Soc. Chim.*, 1901, [iii], 25, 617—618).—Metallic chromium is readily deposited in a steel-grey form on a platinum cathode from a solution of crystalline chromic chloride acidified with hydrogen chloride, or in a silver-white form by electrolysis a solution containing chromium and potassium chlorides in the proportion $\text{CrCl}_3 : 3\text{KCl}$; the current density was 0.15 ampere per sq. cm., and the pressure 8 volts. The metal is not attacked by concentrated sulphuric acid, nitric acid, or potassium hydroxide. T. M. L.

A new Oxide of Chromium, CrO . By JULES FÉRÉE (*Bull. Soc. Chim.*, 1901, [iii], 25, 619—620).—The oxide CrO is obtained as a black powder by the oxidation of chromium amalgam exposed to air. It has a constant composition, and when dissolved in hydrogen chloride liberates an amount of hydrogen corresponding with the equation $3\text{CrO} + 8\text{HCl} = \text{CrCl}_2 + 2\text{CrCl}_3 + 3\text{H}_2\text{O} + \text{H}_2$; when struck with a pestle or when heated in air, it inflames and burns to the green oxide; it is not changed by heating in a vacuum; it is insoluble in nitric acid or dilute sulphuric acid, but dissolves in hydrochloric acid to a blue solution, which becomes green on the addition of nitric acid. T. M. L.

A new Hydrate of Chromium Sesquioxide, $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$. By JULES FÉRÉE (*Bull. Soc. Chim.*, 1901, [iii], 25, 620—622).—By the electrolysis of neutral solutions of chromic chloride, a brown substance

is produced, which Bunsen (*Ann. Phys. Chem.*, 1854, 91, 619) regarded as having the formulæ Cr_4O_5 or Cr_5O_6 ; experiments are now described to show that this is a hydrate, $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$; when heated in air or in a vacuum, it glows at about 400° , gives off water, and is converted into the green oxide.

T. M. L.

Chromium Nitride. By JULES FÉRÉE (*Bull. Soc. Chim.*, 1901, [iii], 25, 618).—Chromium nitride, CrN (Briegleb and Geuther, *Annalen*, 1862, 123, 239), can be prepared in a pure state by heating pyrophoric chromium, obtained by distilling an amalgam at a temperature below 350° , in a current of nitrogen or ammonia gas; it is insoluble in hydrochloric acid, nitric acid, and aqua regia.

T. M. L.

New Hydrate of Normal Sodium Chromate. By HEINRICH SALKOWSKI (*Ber.*, 1901, 34, 1947—1950).—The salt $\text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$ was obtained accidentally from the mother liquors of a solution out of which the salt $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ had been crystallised. It crystallised in triclinic plates and further crops were obtained by seeding saturated solutions of sodium chromate with it. The solubilities of the salt between 17° and 27° are plotted, and compared with the solubilities of the tetra- and deca-hydrates.

R. H. P.

Uranium Amalgam and Pyrophoric Uranium. By JULES FÉRÉE (*Bull. Soc. Chim.*, 1901, [iii], 25, 622—623).—Uranium amalgam is very readily oxidised, but can be prepared by electrolysing uranous chloride in a divided cell; on distilling off the mercury at 241 — 242° , a residue of metallic uranium is left, which inflames spontaneously in the air.

T. M. L.

Cæsium-Antimonious Fluorides and other Double Haloids of Antimony. By HORACE L. WELLS and F. J. METZGER (*Amer. J. Sci.*, 1901, [iv], 11, 451—456).—Several double fluorides of cæsium and antimony were obtained by mixing varying proportions of solutions of cæsium fluoride and antimony fluoride, prepared by treating the respective carbonate and oxide with hydrofluoric acid. The salt $\text{CsF} \cdot 2\text{SbF}_3$ crystallises in beautiful, transparent needles, the salt $\text{CsF} \cdot 3\text{SbF}_3$ in stout, transparent prisms, and the salt $4\text{CsF} \cdot 7\text{SbF}_3$ (?), in transparent plates; the salt $\text{CsF} \cdot \text{SbF}_3$ obtained when the cæsium fluoride is in excess, crystallises in square prisms, and the salt $2\text{CsF} \cdot \text{SbF}_3$ obtained when a large excess of cæsium fluoride is present, in rhombic prisms. The *cæsium antimonious iodide*, $3\text{CsI} \cdot 2\text{SbI}_3$, occurs in two modifications, one of which is brick-red in colour and apparently octahedral in form, whilst the other is yellow and occurs in thin, hexagonal plates. An indefinite *cæsium antimonie fluoride*, $\text{CsF} \cdot \text{SbF}_4 \cdot \text{OH}$, is also described, and crystallises in bundles of transparent needles.

R. H. P.

Gold and Silver Alloys and other materials obtained from Egyptian Tombs. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 1282—1286. Compare this vol., ii, 25).—This communication contains a further account of the analytical researches made on gold and silver alloys and other antique objects taken from Egyptian tombs of various epochs. The data obtained are, however, not suffi-

cient to permit of generalisations being made connecting the composition of the alloys with the date of their manufacture. G. T. M.

Metals of Ancient Egypt : Study of a Metallic Sheath and its Inscriptions. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1901, [vii], 23, 5—32).—This communication is chiefly of archæological interest: the presence of an alloy containing platinum, iridium, and gold amongst the materials forming the sheath has been previously indicated (compare this vol., ii, 318). G. T. M.

Mineralogical Chemistry.

Gold and Silver Tellurides from the Kalgoorlie District (Western Australia). By ADOLPHE CARNOT (*Compt. rend.*, 1901, 132, 1298—1302).—Analyses of samples of tellurides taken from the Lake View Consols and Great Boulder Proprietary mines, show that the following mineral species are present: Sylvanite, $(\text{Au}, \text{Ag})\text{Te}_2$, calaverite, corresponding with the preceding substance but less crystalline, and containing a smaller proportion of silver, kalgoorlite, $(\text{Au}, \text{Ag}, \text{Hg})_2\text{Te}$, and a new sesquittelluride, *coolgardite*, $(\text{Au}, \text{Ag}, \text{Hg})_2\text{Te}_3$, containing very variable proportions of gold and silver, the metals replacing each other isomorphously. These minerals also contain small quantities of copper, nickel, iron, and antimony, and their percentage compositions are tabulated.

G. T. M.

Mohawkite. By JOSEPH W. RICHARDS (*Amer. J. Sci.*, 1901, [iv], 11, 457—458).—Koenig has recently given the name mohawkite to a nickeliferous and cobaltiferous variety of domeykite, $(\text{Cu}, \text{Ni}, \text{Co})_3\text{As}$, from the Mohawk mine, Michigan (this vol., ii, 108). The same name had, however, been previously used by Ledoux (*Eng. Min. J.*, 1900, 69, 414), for a similar [probably the same] mineral from the same mine to which he gave the formula Cu_4As . The latter formula was doubted by Koenig, but is confirmed by the present author, who proposes the name *ledouxite* for a mineral having this composition. The results of his analysis are:

| Cu. | Co. | Ni. | Fe. | As. | Total. | Sp. gr. |
|------|-----|-------|-----|--------|--------|----------|
| 70·8 | 6·4 | trace | 0·0 | [22·8] | 100·0 | 8·07 |
| | | | | | | L. J. S. |

Microlite from Finland. By ADOLF ERIK NORDENSKIÖLD (*Jahrb. Min.*, 1901, i, Ref. 352; from *Geol. För. Förh.*, 1899, 21, 639).—Indistinct crystals of ixiolite and skogbölite from Skogböle, Kimito, Finland, are coated with a yellowish-brown, crystalline layer, 0·5 mm. thick, of microlite. Analysis of this gave:

| Ta_2O_5 . | SnO_2 . | CaO . | FeO . | Ce_2O_3 . | Loss on ignition. | Total. | Sp. gr. |
|---------------------------|------------------|----------------|----------------|---------------------------|----------------------|--------|---------|
| 72·16 | 1·96 | 14·23 | 4·79 | 0·14 | 0·11 | 93·39 | 5·65 |

The deficiency of 6.61 per cent. probably represents alkalis and fluorine.

L. J. S.

Calcareous Concretions of Kettle Point, Ontario. By REGINALD A. DALY (*J. Geol.*, 1900, 8, 135—150).—A description is given of the large spherical concretions which occur in bituminous shale at Kettle Point, at the southern end of Lake Huron. They consist of radially crystallised calcium carbonate, and show also a concentric structure. Analysis of a darker brown ball gave: CaCO_3 , 88.42; MgCO_3 , 2.99; Fe_2O_3 , 0.71; insol. in hydrochloric acid (SiO_2), 4.25; hydrocarbons and water, 3.23 = 99.60. The mode of origin of the concretions is discussed, and the local deformation of the shale around the balls is attributed to the change in volume when the material was deposited from solution.

L. J. S.

Natural History of Marl. By CHARLES A. DAVIS (*J. Geol.*, 1900, 8, 485—497).—Aquatic plants are frequently encrusted with mineral matter, especially calcium carbonate. The absorption of carbon dioxide and the liberation of oxygen by the plant causes the deposition of calcium carbonate from a solution of calcium hydrogen carbonate. A sample of *chara* dried at 100° gave on analysis: CaCO_3 , 76.00; MgCO_3 , 2.359; Fe_2O_3 , Al_2O_3 , 0.722; insoluble in hydrochloric acid, 11.19 (consisting of combustible and volatile matter, 9.243; silica, 1.787; undetermined, 0.160); soluble organic matter by difference, 9.279 per cent. On these grounds, it is suggested that many important deposits of marl may have been formed by the agency of aquatic plants and especially *chara*. In an accompanying paper (*ibid.*, 498—503) by the same author, a description is given of a small lake in Michigan where marl is now being deposited in this way.

L. J. S.

Alumina present in Mineral Waters. By F. PARMENTIER (*Compt. rend.*, 1901, 132, 1332—1333).—The majority of the mineral waters from central France (Vichy) contain notable quantities of alumina, although former analyses have not indicated the presence of this substance. When these waters lose their carbon dioxide, precipitates of crystallised calcium and magnesium carbonates are formed, and finally, when the gas has almost entirely disappeared, a deposit of alumina is produced containing variable quantities of ferric oxide. The addition of lime water to these waters produces a white turbidity which after a time partly disappears. This precipitate consists of calcium and magnesium carbonates mixed with alumina, the carbonates redissolve in the excess of carbonic acid present, whilst the alumina undergoes polymerisation, and gradually collects together as a deposit consisting of closely united filaments.

G. T. M.

Analysis of Red Rain Deposit, which fell in Victoria, Australia, December 26, 1896. By THOMAS L. PHIPSON (*Chem. News*, 1901, 83, 253).—The deposit consisted of exceedingly small grains of various colours, many being flat or tabular with irregular edges; it was very slightly, if at all, magnetic. When treated with hydrochloric acid, it neither effervesced nor evolved chlorine. Analysis yielded the following numbers per cent.: Water, 9.09;

organic matter, 5.21; soluble in hydrochloric acid, 8.00 (containing Fe_2O_3 , Al_2O_3 , SiO_2 , and TiO_2 , 4.61; CaO , MgO , Na_2O , K_2O , and traces of Ni and CO , 3.39). Insoluble in hydrochloric acid, 77.70 (containing SiO_2 , 50.99; Fe_2O_3 and Al_2O_3 , 16.40; CaO , 0.21; Na_2O , K_2O , and trace of Li_2O , 10.10). Before the blow-pipe and in composition the insoluble portion resembles felspar.

D. A. L.

Physiological Chemistry.

Respiration in Annelids. By BOUNHIOL (*Compt. rend.*, 1901, 132, 1348—1351).—The amount of carbon dioxide produced per unit of time by the aquatic worm *Spirographis*, was taken as a measure of its respiratory activity. Under constant conditions, this does not vary greatly in the same animals, but it can adapt itself to changes in their surroundings. With an equal weight of small and large animals, respiration is more active in the former; this is no doubt connected with a greater surface area. If the gills are removed, the amount of gas produced sinks by a quarter, but in a few hours returns to the normal. If the skin is vaselined, the amount of gas again falls, but returns to the normal some hours later. If the temperature of the water is raised within moderate limits, respiration is slightly more active. Light has no influence. W. D. H.

Influence of Boric Acid and Borax on Metabolism in Children. By FRANCIS W. TUNNICLIFFE and OTTO ROSENHEIM (*J. Hyg.*, 1901, i, 186—201).—A series of experiments on children, which seek to show that boric acid and borax are practically harmless.

A. S. GRUNBAUM (*Brit. Med. J.*, 1901, i, 1337) criticises Tunncliffe and Rosenheim's work. The experiments are few, each lasted only 12 days, and the children selected are above the age when milk is the staple article of diet. The fact that the boric acid and borax are rapidly excreted by the kidneys is evidence of their poisonous character. W. D. H.

Influence of Formaldehyde on the Metabolism of Children. By FRANCIS W. TUNNICLIFFE and OTTO ROSENHEIM (*J. Hyg.*, 1901, i, 321—366).—The experiments were made on children in a way similar to those previously recorded with borax (preceding abstract). The children were three in number, aged $2\frac{1}{2}$, 4, and 5 years respectively. The normal course of metabolism was compared with that occurring during a limited period (7 to 14 days) when small quantities of formaldehyde were added to the diet. The general health was not affected, but there is a diminution of phosphorus and fat assimilation. In one child who was weakly, the nitrogenous assimilation was also injuriously affected. There was no intestinal antiseptic action, and the bad effects of the drug are attributed to its effect on pancreatic digestion.

W. D. H

Influence of Lecithins in the Egg in Nutritive Exchanges. By ALEXANDRE DESGREZ and A. ZAKY (*Compt. rend.*, 1901, 132, 1512—1514).—The lecithins of the fowl's egg increase the appetite of animals which receive them either by the mouth or under the skin. These animals rapidly increase in weight. Urea, total urinary nitrogen, and the coefficient of utilisation of nitrogen are increased, but the phosphoric acid in the urine is diminished. W. D. H.

[**Dietary Studies.**] By HARRY S. GRINDLEY, J. L. SAMMIS, E. F. LADD, ISABEL BEVIER, and ELIZABETH C. SPRAGUE (*U.S.A. Dept. Agric. Bull.*, 1900, 91, 1—42).—Statistics are given of the dietaries in certain public institutions for men and for women. Particular attention is paid to cost, nutritive value, and the amount of waste. W. D. H.

The Fat-splitting Ferment of the Stomach. By FRANZ VOLHARD (*Chem. Centr.*, 1901, i, 1296—1297; from *Zeit. klin. Med.*, 42, 414—429).—The mucous membrane of the fundus of the stomach secretes a fat-splitting enzyme, which can be extracted with glycerol. It is weakened and eventually destroyed by pepsin-hydrochloric acid. W. D. H.

Hippuric Acid Metabolism in Man. By CARL LEWIN (*Chem. Centr.*, 1901, i, 1297; from *Zeit. klin. Med.*, 42, 371—397).—A healthy man secretes daily from 0.1 to 0.3 gram of hippuric acid. This amount is increased by feeding on dextrose, by increase in intestinal putrefaction, or by administration of foods rich in nuclein, such as sweetbread, this being, however, attributed to the increase of putrefaction in the intestines, since nucleic acid does not produce the effect. In gout and diabetes, the amount is normal; in febrile conditions, in kidney disease, and in perityphlitis the amount of hippuric acid rises. W. D. H.

Presence of Carbon Monoxide in the Blood. By MAURICE NICLOUX (*Compt. rend.*, 1901, 132, 1501—1504).—The presence of small amounts of carbon monoxide has been shown in the blood of anæsthetised animals, in the blood of normal dogs, and in the Paris atmosphere. It is now stated that this gas (0.11 c.c. in 100 c.c. of blood) occurs in the blood of animals just born. This observation appears to relate to human beings, but there is no clear statement on this point. W. D. H.

Blood of Animals deprived of their Suprarenals. By ISAAC LEVIN (*Amer. J. Physiol.*, 1901, 5, 358—361. Compare this vol., ii, 256).—The results of the experiments show that the suprarenal gland not only forms an internal secretion, but is also excretory. It is strange that the blood of such animals and suprarenal extracts both raise the blood pressure; it may, however, be that the two materials are in other respects antagonistic. W. D. H.

Presence and Localisation of Iodine in the Leucocytes of Normal Blood. By HENRI STASSANO and PAUL BOURCET (*Compt. rend.*, 1901, 132, 1587—1589. Compare Abstr., 1900, ii, 555).—An examination of blood drawn from a dog as rapidly as possible, and

either defibrinated or treated with sodium oxalate, shows that the iodine present is contained solely in the degradation products of the leucocytes. The red corpuscles, when completely freed from leucocytes, contain no trace of this element.

G. T. M.

Rhythmic Activity of the Œsophagus. By PERCY G. STILES (*Amer. J. Physiol.*, 1901, 5, 338—357).—The action of various salts, interpreted by the ionic theory, is described in connection with the rhythm of the isolated œsophagus of the frog. Sodium is essential, but by itself sodium chloride is depressant. The simultaneous presence of calcium and potassium is also necessary; a stimulating rôle is assigned to calcium, and an inhibiting one to potassium.

W. D. H.

A new form of Muscular Irritability. By JACQUES LOEB (*Amer. J. Physiol.*, 1901, 5, 362—373).—Certain salt solutions (1 gram-mol. in 8 or 10 litres) bring about an apparently new form of irritability in muscles, which is termed 'contact irritability.' A muscle which has been treated in this way will contract powerfully when it passes from the salt solution to air, carbon dioxide, oil, sugar solution, &c., or from solutions of glycerol or sugar to air. The salts which act in this way are with one exception sodium salts, the anions of which are capable of precipitating calcium; they are sodium fluoride, carbonate, oxalate, citrate, tartrate, and disodium hydrogen phosphate. If the nerve alone is put into one of these solutions, the muscle begins to twitch and finally goes into tetanus; the contraction ceases when the nerve is removed from the solution. The salts or their ions do not directly stimulate the nerve, but only modify or increase its irritability, for when the same nerve is brought into contact with any solid or liquid body, the muscle resumes its contractions, whilst these gradually cease or diminish when the nerve is again surrounded with air. It is regarded as possible that alterations of motor and sensory reactions in neurotic patients may be due to ionic action.

W. D. H.

Rigor in Frog's Muscles. By N. M. STEVENS (*Amer. J. Physiol.*, 1901, 5, 374—386).—From experiments on the frog's gastrocnemus, the following conclusions are drawn: the energy of *rigor* contraction decreases rapidly with decrease of temperature, being very slight at or below 20°. The energy of secondary heat contractions at 50—63° is less than that of ordinary *rigor* contraction at 20°. A muscle undergoing heat *rigor* does more work when it contracts against a spring than when it is "after loaded" (200 grams). The fact that complete *rigor* at 20° entirely cuts out the first heat contraction at 37—45°, but not that at 50—63° indicates that *rigor mortis* involves coagulation of soluble myogen fibrin, but not of myosin or myogen. The fact that immersion of the muscle in chloretone solution (0.1 to 0.5 per cent.) produces a similar contraction, indicates that chloretone coagulates soluble myogen fibrin, but not the other proteids. A slight contraction produced by weak chloretone solution is compensated by a proportionately greater secondary heat contraction, as in the case of slight *rigor mortis* contractions (Brodie and Richardson). The action of chloretone is very definite and constant as compared with that of

potassium thiocyanate. The nomenclature of the muscle proteids is that introduced by von Fürth. W. D. H.

Origin of Iodine in the Organism. By PAUL BOURCET (*Compt. rend.*, 1901, 132, 1364—1366).—The amount of iodine in various foods was examined. Vegetable food is the main source of iodine in the animal body, and the greater part of this element is returned again by the excretions to complete the biological cycle.

W. D. H.

Osseo-mucoid. By P. B. HAWK and WILLIAM J. GIES (*Amer. J. Physiol.*, 1901, 5, 387—425. Compare this vol., ii, 298).—Lime water extracts from ossein, prepared from partly decalcified ribs and femora of the ox, a substance having the characters of mucin and chondromucoid: it is termed *osseo-mucoid*. This shows, contrary to Young's deduction, that in ossification the connective tissue matrix is not completely removed. Variations in percentage composition indicate the probability that two or more glucoproteids exist in bone. The four analyses showing the most concordant results give the following average percentages: C, 47.07; H, 6.69; N, 11.98; S, 2.41; O, 31.85. Phosphorus is absent. Between 1 and 1.6 per cent. of the sulphur may be split off as sulphuric acid on boiling with dilute hydrochloric acid. The energy liberated on oxidation of mucin substances is less than that for any form of proteid except fibroin.

W. D. H.

Absorption and Secretion. By MAX. OKER-BLOM (*Pflüger's Archiv*, 1901, 85, 543—575).—This is the fifth of a series of papers on the physico-chemical relationships of animal tissues and juices. The importance of osmotic pressure and kataphoresis in the phenomena of absorption and secretion is pointed out at considerable length and with experimental data.

W. D. H.

Bile of Polar Animals. I. Bile of the Polar Bear. By OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1901, 32, 435—466).—Specimens of bile from polar bears were collected on certain Arctic expeditions, and received in alcohol. Numerous analytical details are given. The principal pigment is a brownish-yellow one which does not give Gmelin's reaction or any spectroscopic bands; it was found also in gall stones from these animals. There are also small quantities of bilirubin and urobilin. Particular attention is drawn to the presence of an unknown organic substance, which is reducing and rich in sulphur, to the presence in large quantities of a lecithin-like material rich in phosphorus, to the absence of glycocholic acid, and to the relatively high percentage of sulphates in the ash.

W. D. H.

Composition of a Liquid obtained by Tapping. By F. MALMÉJAC (*J. Pharm.*, 1901, [vi], 13, 459—460).—A liquid (890 c.c.) obtained by tapping a patient in the tenth intercostal space gave the following results on analysis, in grams per litre. Sp. gr. 1.013; reaction distinctly alkaline. Sodium chloride, 6.6; phosphoric acid, 0.08; acetone, 0.206; urea, 2.5; total proteids, 25.432, of which 23.304 was serum-albumin. Urobilin was also present in large

amount ; also a few pus globules. Alcohol, aldehyde, uric acid, globulin, peptones, sugar, bile, indican, and blood were absent. The liquid had no odour ; its colour resembled that of coffee. M. J. S.

Use of Silicotungstic Acid as a Reagent for the Alkaloids in Urine ; Variations in Alkaloidal Nitrogen. By H. GUILLERMARD (*Compt. rend.*, 1901, 132, 1438—1440).—The alkaloids in urine are readily precipitated in the form of an amorphous, rose coloured powder, by silicotungstic acid in presence of hydrochloric acid after removal of proteids. The precipitate contains creatinine, xanthic bases, a yellow, amorphous, alkaloidal colouring matter, a non-crystallisable substance which seems to form the non-dialysable basic part of urine, and a volatile substance which has a strong odour of urine and forms a soluble crystallisable platinichloride. The nitrogen may be estimated before precipitation with the silicotungstic acid, and in the precipitate, and thus the ratio of alkaloidal nitrogen and total nitrogen is ascertained. The total amount and the relative amount of "alkaloidal nitrogen" eliminated in 24 hours by a normal subject varies considerably with the diet, and is highest with a flesh diet and lowest with a milk diet. In febrile diseases, even on a milk diet, there is a marked increase in the absolute and relative amounts of alkaloidal nitrogen eliminated. In Bright's disease, on the other hand, the figures are considerably below the normal, but can be brought back to normal by a milk diet. In diabetes, the figures are below normal, whilst in diseases of the nervous centres they are usually much above normal. In other chronic maladies, such as syphilis, chronic rheumatism, chlorosis, &c., there are no definite deviations from the normal. C. H. B.

Behaviour of Pentoses, especially *l*-Arabinose, in the Animal Body. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1901, 32, 393—412).—The experiments described chiefly relate to *l*-arabinose. This substance is well absorbed in rabbits, and about 18 per cent. of it passes unchanged into the urine. It causes, more or less, an accumulation of glycogen in the liver. There is, however, no ground for supposing that the glycogen is directly formed from the arabinose. Whether arabinose is carbohydrate-sparing, fat-sparing, or proteid-sparing is doubtful. After feeding on arabinose, the muscles contain a laevorotatory substance, the nature of which was not made out.

W. D. H.

Behaviour of the three Arabinoses in the Animal Body. By CARL NEUBERG and JULIUS WOHLGEMUTH (*Ber.*, 1901, 34, 1745—1749).—The authors have followed the fate of the three arabinoses when given to rabbits which were being fed on a diet free from carbohydrate ("diabetes-milk"). The arabinose excreted in the urine was estimated as diphenylhydrazone (*Abstr.*, 1900, i, 539). After being fed in turn with each of the three arabinoses (5—10 grams), 14·5 per cent. of *l*-arabinose, 31·2 of *d*-arabinose, and 28·5 of *r*-arabinose respectively appeared in the urine. In the case of *r*-arabinose, some 5 per cent. of *d*-arabinose was also present in the urine with the inactive isomeride. Subcutaneous injection led to

similar results. Injection of the sugar into the auricular vein showed no such contrast between the excretion of the three isomerides in the urine. The *lævo*- is accordingly more readily attacked than the dextro-sugar; *r*-arabinose is partially decomposed into its components, of which more of the dextro-sugar escapes attack, and consequently appears, together with the *r*-arabinose, in the urine. Only from *l*-arabinose, and not from *d*- or *r*-arabinose, could the rabbits form glycogen. Feeding with the sodium salts of the three arabonic acids showed similar results. Attention is drawn to the fact that, physiologically, *l*-arabinose and dextrose are closely allied, whilst chemically dextrose and *d*-arabinose are more nearly related. K. J. P. O.

Physiological Action of Carone. By ENRICO RIMINI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 435—441).—Experiments with frogs, mice, and guinea pigs show that the physiological action of carone is not very strongly marked, and is explained mainly by paralytic phenomena, first of the voluntary muscular movements, and afterwards of the respiration. The heart resists the action of carone when the latter reaches it by means of the circulation, but if the compound is placed in immediate contact with the cardiac muscle, an appreciable diminution takes place in the number of the contractions, until the final stoppage of the heart which occurs very soon, and is always in a condition of semi-diastole. The fact that carone is not capable of causing epileptic convulsions in mammals, and hence differs in its action from the saturated dicyclic ketones isomeric with camphor, is explained by the author as probably due to a transformation of carone in the organism, similar to that produced by dilute sulphuric acid, which converts it into oxytetrahydrocarvone. T. H. P.

Influence of Asphyxia on the Glycogenic function of the Liver. By JOSEF SEEGEN (*Chem. Centr.*, 1901, i, 1297; from *Centr. f. Physiol.*, 25, 65—69).—In normal animals, there is a *postmortem* increase in the sugar of the liver. In dogs and men killed by asphyxia, this does not occur; in such cases, the vitality of the liver cells is lessened. In such cases also, the amount of glycogen is very small.

W. D. H.

Action of Iron in Anæmia experimentally produced. By FRANZ MÜLLER (*Virchow's Archiv*, 1901, 164, 436—492).—In cats, inorganic iron is for the most part absorbed into the blood stream. In dogs rendered anæmic by bleeding, it causes an increase of hæmoglobin. The iron given is used in the bone marrow for the making of the precursors of the blood pigment. It acts as a formative stimulus ("formativer": Reiz, Virchow).

W. D. H.

Action of Strychnine on the Spinal Cord of Rabbits. By HOBART A. HARE (*Amer. J. Physiol.*, 1901, 5, 333—337).—In rabbits, strychnine does not chiefly affect the anterior part of the animal's body, as stated by some observers. The hind legs are affected very promptly, and the exhaustion paralysis here is very marked, whereas the fore limbs speedily regain their power.

W. D. H.

Antidote for Cyanide Poisoning. By OTTO HERTING (*Zeit. angew. Chem.*, 1901, 585—586).—See this vol., ii, 534.

Chemistry of Vegetable Physiology and Agriculture.

Oligonitrophilous Microbes. By MARTINUS W. BEYERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 5—9).—Experiments are described which show that various species of *Cyanophyceæ* will develop in culture liquids containing the mineral constituents of foods, but free from nitrogen compounds; these organisms assimilate nitrogen from the air, and their development is prevented by the presence of nitrogen compounds in the culture liquids.
R. H. P.

Photobacteria as a Reactive in the Investigation of the Chlorophyll Function. By MARTINUS W. BEYERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 45—49).—Photobacteria can be used to show when the chlorophyll of leaves is functioning, for if leaves in contact with a culture of photobacteria are excluded from any source of oxygen, the bacteria will only phosphoresce when the chlorophyll is functioning.
R. H. P.

Biochemical differentiation of the two principal Vinegar Ferments. By GABRIEL BERTRAND and R. SAZERAC (*Compt. rend.*, 1901, 132, 1504—1507).—The two best known vinegar ferments, *Mycoderma aceti* and the sorbose bacterium (Brown's *Bacterium xylinum*), differ markedly in their behaviour towards glycerol solutions. A pure culture of the first of these, introduced into a sterilised nutritive solution of glycerol, has practically no action on the alcohol, and at the end of three months the solution fails to reduce Fehling's solution. On the other hand, a specimen of the second ferment placed in a similar solution rapidly transforms the glycerol into dihydroxyacetone, the amount of this ketone produced in 2—3 days being sufficient to precipitate an appreciable quantity of cuprous oxide on the addition of copper potassium tartrate.
G. T. M.

Yeast Trypsin. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1901, 32, 419—424).—The author contests Salkowski's claims to priority in the discovery of a tryptic enzyme in yeast (*Abstr.*, 1889, 1027).
J. J. S.

Rate of Nitrification of some Fertilisers. By W. A. WITHERS and GEORGE S. FRAPS (*J. Amer. Chem. Soc.*, 1901, 23, 318—326. Compare Müntz and Girard, *Abstr.*, 1892, 96; and Johnson, Jenkins, and Britton, *ibid.*, 1900, ii, 506).—Sandy soil (3000 grams) was mixed with different amounts of dried blood, containing 1, 0.5, and 0.25 gram of nitrogen respectively, and kept at about 27° in the dark for 14 days, the percentage of moisture being kept constant. It was found that

as the dilution of the blood with soil increased, there was a distinct increase in the amount of nitrogen nitrified. Addition of calcium carbonate increased the amount of nitrogen nitrified from 100 to 156. The conclusion is drawn that 30 lbs. of nitrogen per acre is a liberal application, especially in the case of substances which, like dried blood, are insoluble in water and become imperfectly mixed with the soil.

Experiments on the rate of nitrification are described, in which the manures, in quantities containing 0.6 gram of nitrogen, were mixed with sandy clay soil (1000 grams) and kept for 3 weeks in darkness. In the case of all the manures except ammonium sulphate (namely, dried blood, cotton seed meal, dried fish, tankage, bat guano, and bone), the order of nitrification accorded with the results of vegetation experiments, the results obtained by the permanganate method, and, with the exception of bone, with those of the pepsin hydrochloric acid method (Johnson, Jenkins, and Britton, *loc. cit.*). Addition of calcium carbonate in every case except bone, considerably increased the amount of nitrogen which nitrified; in the case of ammonium sulphate, the quantity of nitric nitrogen formed was 2,390, taking the amount in absence of calcium carbonate as 100. The rate of nitrification of bone was diminished by calcium carbonate.

The comparatively slow nitrification of ammonium sulphate is attributed to the presence of micro-organisms, which act more readily on organic nitrogen. Or the presence of ammonium sulphate may hinder the activity of the nitrifying organisms. Boname found that ammonium sulphate is nitrified very slowly during the first and second months, but very rapidly during the third month; these results are directly opposed to those of Müntz and Girard, and of Schlœsing.

N. H. J. M.

Processes of Denitrification. By OTTO LEMMERMANN (*Bied. Centr.*, 1901, 30, 368—369; from *Habilitationsschr. Jena*, 1900).—The functions of the denitrifying bacteria, of which 23 varieties are now known, are controlled by the absence or presence of suitable carbonaceous matter and oxygen, when the conditions are in other respects normal.

The results of experiments made in Halle, Lauchstädt, and elsewhere, indicate that in practice denitrification has not the importance which has been ascribed to it. The unsatisfactory results sometimes obtained with stable manure cannot to any extent be due to the liberation of free nitrogen, and are more probably owing to direct injury to the plants by the absorption of large amounts of organic matter.

N. H. J. M.

Denitrification in Soil. By G. AMPOLA and C. ULIANI (*Gazzetta*, 1901, 31, i, 185—221. Compare *Abstr.*, 1899, ii, 444).—The authors discuss the work done up to the present on the denitrification question, and describe experiments showing that, if the soil fulfils the conditions necessary for denitrification, that is, if it contains bacteria, nitrate, and assimilable organic material, the nitrate is completely reduced to free nitrogen. Hence, stable manure and sodium nitrate

should not be applied simultaneously, but the former should be allowed to reach its full maturity in the soil before the latter is added. A large number of experiments have been made on the cultivation of wheat, beet, vetches, tobacco, and geraniums on plots, (1) without manure, (2) with calcium nitrate and mineral superphosphate, and (3) with sodium nitrate and mineral superphosphate. The results obtained with wheat and beetroot show that: (1) manuring with calcium nitrate gives a larger product than when the sodium salt is employed; (2) this result is more marked in the case of an exhausted soil, but is quite evident with a soil containing in itself a large proportion of fertilising substances; (3) the question of denitrification must be divided into two distinct parts, according as the fermentation takes place in connection either with chemical manuring with sodium nitrate or with calcium nitrate, which is the final product of nitrification. The smallness of the amount of nitrogen made use of by the plant when sodium nitrate and stable manure are applied simultaneously is shown by the experiments mentioned above to be due to denitrification. Calcium nitrate is a better manure than sodium nitrate, and the former also offers far greater resistance to denitrifying micro-organisms than does the sodium salt.

T. H. P.

Evolution of Sulphur and Phosphorus during the commencement of Germination. By GUSTAVE ANDRÉ (*Compt. rend.*, 1901, 132, 1577—1579).—The results of experiments with haricots showed that the minimum weight of the dry organic matter is reached at the time of the apparent end of germination (13 days). The weight of the ash increased during this period from 4.66 (the amount in 100 seeds) to 7.53 grams. At the end of 20 days, the weight of the plant was 21.4 per cent. more than that of the seeds.

During normal germination, the total sulphur increases regularly from the commencement, the increase being about 50 per cent. by the time the weight of the seedling has reached that of the original seed.

The phosphorus in the form of phosphates increases during germination, whilst the total phosphorus remains stationary until the nitrogen increases.

N. H. J. M.

Sensibility of higher Plants to the action of Potassium Salts. By HENRI COUPIN (*Compt. rend.*, 1901, 132, 1582—1584).—Young wheat plants were grown in solutions of potassium salts and in distilled water. The strongest solution contained 0.0005 gram of potassium phosphate in 100 c.c., and there were twelve other solutions containing from 1/2 to 1/4096 of this amount. A comparison of the length of the third leaf in each case showed the most dilute solutions, beginning with the twelfth, which contained 0.000244 mg. of the salt, are without effect. Experiments made with other potassium salts showed that the limits at which they ceased to have any effect were as follows: K_2CO_3 , 0.0001; K_2SO_4 , 0.0008; KCl, 0.003; and KNO_3 , 0.004 milligram.

N. H. J. M.

Investigations on the Roots of Plants. By HERMANN MÜLLER-THURGAU (*Bied. Centr.*, 1901, 30, 398—399; from *Jahresber. Wadens-wei*, 8, 79. Compare Abstr., 1900, ii, 361).—Further evidence has been obtained that roots utilise certain substances directly for their

own development and that in too dilute solutions the growth of roots is less abundant. Solutions which are too concentrated retard root production. Solutions containing 0.1 per cent. of dissolved salts gave better results than 0.05 per cent. solutions; 0.2 per cent. solutions did not give more root growth than the 0.1 per cent. solution, and may even give less, and a 0.3 per cent. solution was found to be injurious.

N. H. J. M.

Occurrence of Maltol in the Needles of the Silver Fir (*Abies Alba*).—By W. FEUERSTEIN (*Ber.*, 1901, 34, 1804—1806).—Maltol, $C_6H_6O_3$, can be extracted from the needles of the silver fir (*Abies alba*) by macerating with water, and is identical with that prepared from malt by Brand (*Abstr.*, 1894, i, 270), and by Kiliani and Bazlen (*Abstr.*, 1895, i, 80); it crystallises from dilute alcohol in long, silky needles and melts at 159°.

T. M. L.

Conditions of the Production of Proteids in Plants. By ADOLF MAYER (*Landw. Versuchs-Stat.*, 1901, 55, 453—461. Compare *Abstr.*, 1893, ii, 224).—Rye was grown in pots, without and with gradually increasing amounts of ammonium nitrate. The air-dried substance, without nitrogenous manure, contained 1.28 per cent. of nitrogen as crude proteid, and 0.83 per cent. of proteid nitrogen by Stutzer's method, whilst the plants manured with 22.5 grams of ammonium nitrate contained 3.23 and 1.30 per cent. respectively. The nitrogen as nitrates in the air-dried plants increased from 0.07 to 0.50 per cent. The pure proteids did not, therefore, increase in the same proportion as the crude proteids, and the plants which received the largest amount of ammonium nitrate contained a good deal of it unaltered.

Similar experiments with peas, showed that whilst the crude proteid nitrogen increased from 2.20 to 4.20, the increase in pure proteid nitrogen was very much less (1.61—1.87 per cent.).

Field experiments are described in which oats were grown (1) without manure, and (2 and 3) with sodium nitrate (11.5 and 22.5 kilos. per acre respectively). The following amounts of nitrogen were found in the air-dried substance (total and proteid nitrogen by Jodlbauer's and Stutzer's methods):

| | Total N. | Proteid N. | N. as N_2O_5 . |
|---|----------|------------|------------------|
| 1 | 1.80 | 0.72 | 0.036 |
| 2 | 2.71 | 0.88 | 0.68 |
| 3 | 2.23 | 0.90 | 1.21 |

N. H. J. M.

Toxic Value of Mercuric Chloride and its Double Salts. By JUDSON F. CLARK (*J. Physical Chem.*, 1901, 5, 289—316).—It has been generally considered that the addition of acids and of various salts increases the toxic value of mercuric chloride owing to decrease in the precipitation of the mercuric chloride by proteids. The author has investigated the question more fully, and determined the concentration of the mercuric chloride which inhibits the growth of various fungi, seedlings, and bacteria, employing decoctions of sugar beet and also liquids free from proteids as media. The results

are expressed by curves which give the inhibitory concentration against quantity of added salt. The following general results appear from these curves: the first additions of salt cause an increase of the toxic value, which reaches a maximum, further addition decreases the toxic value until a minimum is attained after which a further increase, ascribable to the actual effect of the salt itself, occurs. The author considers that the increase in toxic effect is due to the formation of HgCl_4^- ions; the later decrease, to the decrease of the dissociation, and hence to the decrease in these ions. The usual instructions for adding sodium chloride to mercuric chloride for antiseptic purposes recommend a quantity of the former which would considerably lower the toxic value of the disinfectant (Abstr., 1899, ii, 627).

L. M. J.

Cultivation of Wheat. By ITALO GIGLIOLI (*Cultura del Frumento. Portici*, 1901, pp. xx and 159).—Field experiments on wheat have been made at Suessola (Naples) during the last thirteen years. Since the first year of the experiments, maize has been grown after wheat each season.

The continuously manured plots produced 10·2 hectolitres of grain and 2,070 kilos. of straw per hectare. With ammonium sulphate, the yield of grain and straw was increased to 17·6 hectolitres and 2,750 kilos. respectively. The highest yield was obtained with horse-dung and ammonium sulphate (21·3 hectolitres of grain and 4,080 kilos. of straw).

The author has previously called attention to the importance of preserving urine by adding sulphuric acid to it and employing the mixture as manure, and in the experiments now described it was found that "sulphuric urine" produced an effect similar to that of ammonium sulphate. Good results were obtained with sodium nitrate in conjunction with horse-dung. Basic slag was found to have more effect than mineral phosphates.

Leucite in conjunction with basic slag, ammonium sulphate, and sodium nitrate produced 16·95 hectolitres of grain and 3,670 kilos. of straw per hectare.

Electricity, especially voltaic, produced a marked increase on the plots which received horse-dung.

The application of manganese dioxide, in conjunction with various manures, produced a decided increase in several cases, as compared with the manures without manganese.

N. H. J. M.

Wheat and Vine Culture. By VINCENZO OLIVERI and F. ROMANO (*Gazzetta*, 1901, 31, i, 253—262).—With the view of arriving at a system of rational manuring of soil for wheat and vine growing, the authors have carried out analyses of the grain, straw, and chaff of wheat, and of the wood and the various parts of the fruit of vines. Tables are given recording the results obtained.

T. H. P.

Alinit Experiments with Oats. By BERNARD SCHULZE (*Bied. Centr.*, 1901, 30, 421; from *Jahresber. agrik.-chem. Versuchs-Stat. Breslau*, 1899, 20).—Negative results were obtained when alinit was applied alone and with dextrose or straw extract. The soil contained very little nitrogen.

N. H. J. M.

Peas, Beans, and Vetches and their Mill Products. By ALBERT KOEHLER (*Landw. Versuchs-Stat.*, 1901, 55, 401—434).—A summary of the results of analyses of the seeds and their products, and also of the feeding experiments made by different investigators.

N. H. J. M.

Vegetation Experiments in 1899. By JOSEPH HANAMANN (*Bied. Centr.*, 1901, 30, 419; from *Zeit. landw. Versuchswesen Oesterr.*, 1900, 3, 575. Compare Abstr., 1900, ii, 41).—Mustard was grown in the pots previously employed for barley, without further addition of manure.

The amounts of phosphoric acid taken up from the different soils by the plants, and also the amounts dissolved by 5 per cent. formic and by 2 per cent. citric acid, are given in a table. The results indicate that 5 per cent. formic acid is the more suitable solvent for indicating approximately the amount of available mineral matters in the soil.

N. H. J. M.

Experiments with Calcium Carbonate on Serradella. By BERNARD SCHULZE (*Bied. Centr.*, 1901, 30, 421—422; from *Jahresber. agrik.-chem. Versuchs-Stat. Breslau*, 1899, 23).—The yield of serradella was reduced from 104.75 grams to 67.5, 39.7, 10.95, and 0 gram (dry matter) respectively by adding 0.5, 1, 2, and 5 per cent. of calcium carbonate to the soil. Similar results were obtained with lupins. The soil was intentionally kept dry to resemble the conditions in fields; possibly calcium carbonate would be less injurious in presence of more moisture.

N. H. J. M.

Nutrition of Sugar Beet. By JULIUS STOKLASA (*Bied. Centr.*, 1901, 30, 393—395; from *Bl. Zuckerrübenbau*, 1900, 161 and 178. Compare Abstr., 1899, ii, 45).—During the first period of the development of sugar beet, the leaf contains 1.3 and the roots 2.8 per cent. of nuclein; in the roots, the amount decreases to 1.5 per cent. as the amount of sugar increases. The leaves of roots with high percentage of sugar contain much ash with much phosphoric acid and potash. Potassium and sodium oxides seem to play an important part in neutralising organic acids, especially oxalic acid, which amounts to 8 per cent. of the dry matter of the leaves. Potassium chloride acts in the production of carbohydrates, such as hemicellulose, cellulose, and lignin substances containing pentosans, of which the beet contains more than 14 per cent. in the first year of growth (compare Abstr., 1900, ii, 100). Lime is of importance in the production of lignocellulose and the skeleton, the ash of which contains 75 per cent. of lime. The root activity of the sugar beet has mainly an electro-negative character, whilst that of some cereals, such as barley, has a more electro-positive character. The pure ash of sugar beet contains about 68 per cent. of alkali oxides and 12.7 per cent. of phosphoric and silicic acids, whilst the ash of barley contains 24 per cent. of alkali oxides and 61 per cent. of phosphoric and silicic acids.

N. H. J. M.

Milk Proteid as Food. By BACKHAUS and R. BRAUN (*Bied. Centr.*, 1901, 30, 372—375; from *Ber. Landw. Inst. Univ. Königsberg*, 5, 34—59).—The results of feeding experiments with a dog showed that proteid in the form of casein gave better results as regards increase of weight than meal. Insoluble casein had the same effect as the soluble preparation.

Metabolism experiments with rabbits showed that 94·1—99·48 per cent. of milk proteid was utilised.

Soluble proteid is best obtained by mixing trisodium phosphate (6—8 per cent.) with dry proteid; a mixture of sodium phosphate and citrate and borax is also suitable. Borax is beneficial as a preservative, and it was found, by experiments with rabbits and mice, that very large amounts of borax mixed with casein may be consumed without injury. In some cases, the animals died, but it is uncertain whether this was due to borax.

N. H. J. M.

Feeding with Molasses and Molasses-foods. By AL. VELICH (*Zeit. Zuckerind. Böhm.*, 1901, 25, 372—383 and 415—420).—The earliest feeding experiments with molasses are those of Stöckhardt (1850), in which sheep were fed with hay, and with hay and molasses; the results were satisfactory. In 1860, Henneberg and Stohman, in experiments with bullocks, also obtained good results, and found that 8 kilos. of molasses per 1000 kilos. of live weight was the greatest amount completely utilised, and that this quantity was not injurious.

The results of more recent experiments, both with molasses and with mixtures of molasses with various substances, are discussed. The conclusion is drawn that molasses is to be recommended for feeding cattle and horses, but that it should at first be given in gradually increasing amounts.

N. H. J. M.

Seaweed as Food. By P. R. SOLLEID (*Bied. Centr.*, 1901, 30, 375—377; from *Tidsskr. Norsk. Landbr.*, 1901, 13—30).—Analyses of the following varieties were made: (1, *a* and *b*) *Fucus serratus* (2, *a* and *b*), *F. vesiculosus*, (3) *Ascophyllum nodosum*, (4) *Laminaria saccharina*, (5) *Sarcophyllis edulis*.

| | Water. | Crude proteid. | Digestible proteid. | Pentosans. | Crude fibre. | Fat.* | | Ash. |
|-----|--------|-------------------|------------------------|------------|-----------------|-------|------|-------|
| | | | | | | 1. | 2. | |
| 1a. | 10·84 | 9·63 | 1·75 | 7·68 | 5·40 | — | 1·30 | 24·16 |
| 1b. | 11·08 | 8·33 | 0·75 | 6·85 | 9·95 | 1·49 | — | 17·52 |
| 2a. | 16·43 | 11·63 | 4·56 | 7·59 | 8·15 | 2·26 | 1·53 | 22·27 |
| 2b. | 12·40 | 6·88 | 0·13 | 9·41 | 6·55 | 2·80 | 2·39 | 17·06 |
| 3. | 13·00 | 9·44 | 3·38 | 10·21 | 4·13 | 3·95 | 3·03 | 21·51 |
| 4. | 8·42 | 10·63 | 6·00 | 6·22 | 5·52 | 0·70 | 0·49 | 13·33 |
| 5. | 14·12 | 16·44 | 12·50 | 2·86 | 3·15 | 0·28 | 0·24 | 19·08 |

1a, 2a, and 3 were dried in their natural state; the rest were first washed with fresh water, with the result that, not only the amount of ash, but also of the digestible proteid were reduced.

It is thought that the plants would be suitable for feeding if mixed with nitrogenous refuse such as herrings and whale meal.

N. H. J. M.

* Extracted (1) with ether, (2) with light petroleum.

[Preservation of Farmyard Manure.] By PAUL WAGNER (*Bied. Centr.*, 1901, 30, 370—371; from *Hess. Landw. Zeit.*, 1900, 435).—To prevent loss of nitrogen in stable manure, the activity of nitrifying organisms should be promoted, in order that their action may predominate over that of the denitrifying organisms. Another method would be to induce a rapid and complete transformation of the ammoniacal nitrogen of the manure into proteid nitrogen, after ascertaining whether the nitrogenous compounds so produced are sufficiently active. N. H. J. M.

Composition of Odessa Sewage. By THEODOR T. SELIWANOFF, CHOINA, MOTCHAN, and BONDAREFF (*Landw. Versuchs-Stat.*, 1901, 55, 463—474).—The sewage, which is employed for irrigation, is more concentrated than the sewage of Paris, Berlin, and Breslau. Its composition varies considerably, not only on different days, but at different hours, and there seems to be no relation between the composition and the temperature, or the amount of rain. The insoluble dry matter varies in amount more than the dissolved matter, and of the single constituents, chlorine varies the most. N. H. J. M.

Drain-water and Salt Swamps of the Odessa Irrigation Fields. By THEODOR T. SELIWANOFF (*Landw. Versuchs-Stat.*, 1901, 55, 475—478).—The drainage is shown to be very suitable for irrigation, except as regards phosphoric acid, which is absent. The analysis of the drainage showed that it contains N as NH_3 , 0.0035; N as N_2O_5 , 0.378; and K_2O , 0.185 per thousand.

By means of drainage, and by slightly raising the level of the ground, much of the low-lying land, which contains large amounts of sodium chloride, can be rendered fertile. N. H. J. M.

Analytical Chemistry.

Preparation of Strictly Tenth-Normal, Fifth-Normal, &c., Hydrochloric or Nitric Acid. By RICHARD K. MEADE (*J. Amer. Chem. Soc.*, 1901, 23, 343—347. Compare this vol., ii, 342).—The sulphuric acid liberated from a solution of pure crystallised copper sulphate is mixed with an equivalent quantity of barium chloride or barium nitrate and the whole is diluted to a litre, and an amount of water is added sufficient to compensate for the volume of the barium sulphate. For instance, if 12·487 grams of crystallised copper sulphate have been taken, 12·215 grams of crystallised barium chloride or 13·076 grams of barium nitrate will be required, and the volume of the precipitate will amount to 2·6 c.c.; a *N*/10 hydrochloric or nitric acid will be the result.
L. DE K.

Estimation of Hydrogen in Gas Mixtures. By FRANCIS C. PHILLIPS (*J. Amer. Chem. Soc.*, 1901, 23, 354—356).—The hydrogen is burnt as usual by passing the mixture of the gas with air over

palladium asbestos, but to prevent the asbestos from becoming damp, the author heats the tube containing it in hot water. In order that the gas measurements may not be affected by the close proximity of the burette to the source of heat, the following arrangement is recommended. A brass cylinder, 30 cm. long and 18 cm. wide, open at both ends, its rims being strengthened by wires, is silvered on both sides. Its inner surface has three supports riveted to it, on which rests a cup-shaped, brass vessel 18 cm. deep and 12 cm. wide, silvered on the outside. This vessel is filled with water, which is raised to nearly the boiling point by means of a small gas flame. The tube containing the palladium asbestos is bent into a U shape, and this is placed in the water. The operation is then conducted as usual.

L. DE K.

Influence of Selenium on Certain Tests for Arsenic. By OTTO ROSENHEIM (*Chem. News*, 1901, 83, 277—280).—Selenium may be occasionally present in substances to be tested for arsenic. When using Marsh's apparatus connected with a wash-bottle containing lead acetate, the presence of selenium does not necessarily interfere with the formation of true arsenical mirrors, and it is only when the amount of selenium is comparatively large that a deposit is obtained in the generating flask of arsenic triselenide, and the formation of arsenical mirrors is thus totally or partially prevented.

Gutzeit's test, where the material is treated with hydrochloric acid and zinc, and the resulting hydrogen tested with solution of silver nitrate or mercuric chloride, is also similarly interfered with by large quantities of selenium. Reinch's test is also interfered with by selenium, but the author states that it may be rendered useful by first heating the liquid repeatedly with silver foil, which gradually removes the selenium; the arsenic may then be deposited as usual on copper. Bettendorf's stannous chloride test is interfered with by the presence of selenium, and Bloxam's electrolytic process does not appear quite safe, as traces of hydrogen selenide are formed.

L. DE K.

Estimation of the availability of Organic Nitrogen in Commercial Fertilisers. By JOHN PHILLIPS STREET (*J. Amer. Chem. Soc.*, 1901, 23, 330—338).—After estimating the total nitrogen, a quantity of material equivalent to 0.075 gram is, if necessary, washed with cold water, and then heated for 30 minutes in an Erlenmeyer flask on the steam-bath with 100 c.c. of a solution of potassium permanganate (16 grams per litre). The undissolved matter is collected, washed with 150 c.c. of water, and the nitrogen again estimated. The difference between the two determinations represents the available nitrogen. It does not, of course, claim to show the exact amount of organic nitrogen available to the plant, but it serves as a useful means of distinguishing high class products from comparatively worthless ones.

A lengthy table is appended, which shows that in the case of the more valuable manures (dried blood, dried fish, tankage) the greater portion of the nitrogen is soluble, but that little is soluble in the case of garbage, hair, leather, &c.

L. DE K.

Improving the Delicacy of the Diphenylamine Test for Nitric Acid. By RUDOLF HEFELMANN (*Zeit. öffentl. Chem.*, 1901, 11, 200).—The author uses the following process for the detection of nitrates in milk. One c.c. of milk serum is put into a wine glass and a solution of diphenylamine in sulphuric acid is carefully run down the side of the glass. A few small particles of pure sodium chloride are sprinkled over the milk serum; these, when sinking, come into contact with the sulphuric acid and evolve hydrogen chloride, which then causes a beautiful blue zone if nitrates are present. The test may be also applied to waters.

L. DE K.

Detection and Estimation of Nitrates in Water with Brucine and Glacial Formic Acid. By PAUL CAZENEUVE and H. DÉFOURNEL (*Bull. Soc. Chim.*, 1901, [iii], 25, 639—640).—A delicate test for the presence of nitrates in drinking water consists in evaporating a litre of the water, redissolving in 20 c.c. of distilled water, and evaporating again with 0.05 gram of brucine. If nitrates are present, the addition of glacial formic acid and a little water causes the development of a yellow colour, passing into pink in about 12 hours. This method has the advantage that formic acid, unlike sulphuric acid, is usually quite free from nitrates.

T. M. L.

Detection and Estimation of Nitric Acid in Combination with the Alkali Metals. By EDGAR P. PERMAN (*Chem. News*, 1901, 83, 193).—The author has observed that alkali nitrates when heated with lead sulphate or alum yield alkali sulphates with evolution of red nitric fumes.

The process may be made quantitative by heating the nitrate with anhydrous potash alum for a few minutes at a low red heat, when the loss in weight will represent nitric pentoxide. Chlorides should be absent, as they would cause the formation of volatile aluminium chloride.

L. DE K.

Bleaching of Magnesium Pyrophosphate by Conversion into Magnesium Pyrosulphophosphate. By HENRI PELLET (*Ann. Chim. anal. appl.*, 1901, 6, 211—212).—When blackish-looking magnesium pyrophosphate is dissolved in a little strong sulphuric acid, and then evaporated and gradually heated to redness, a perfectly white residue is obtained which, however, is no longer magnesium pyrophosphate, but has retained a molecule of sulphuric anhydride; the author calls it magnesium pyrosulphophosphate. For calculating it into magnesium oxide or phosphoric oxide, the factors 0.265 or 0.470 are used respectively.

L. DE K.

Estimation of Soluble Lead in Resinate-Driers. By RUDOLF HEFELMANN (*Zeit. öffentl. Chem.*, 1901, 11, 202).—As only that portion of the metal which is combined with the resin acids or the acids of linseed oil is of value, all suspended metallic oxides, &c., being worthless, the following method has been devised. Twelve to fifteen grams of the resinate are extracted with chloroform, the liquid is poured off, filtered into a 250 c.c. flask, and diluted to the mark. Fifty c.c. are mixed in an Erlenmeyer flask with an excess of a saturated solution of hydrogen sulphide in absolute alcohol, which precipitates the lead. The

sulphide is collected, washed with a mixture of alcohol and chloroform, converted into sulphate, and weighed. Manganese is estimated in another part of the chloroform solution after evaporation and burning off the organic matters.

L. DE K.

Volumetric Estimation of Iron and Tin by means of Stannous Chloride. By CONSTANTIN ZENGELIS (*Ber.*, 1901, 34, 2046—2050. Compare Campbell, *Zeit. angew. Chem.*, 1888, 168).—The method depends on the use of sodium molybdate as indicator, this, in the presence of the least excess of stannous chloride, yielding the characteristic molybdenum-blue. The blue colour is also given by cuprous chloride, but not by ferrous chloride. For the estimation of iron, the iron is converted into the ferric state and is then titrated with standard stannous chloride until the colour becomes very faint, the solution is boiled for a few minutes and a drop added to a drop of the indicator in a small porcelain dish; if no blue colour is developed, a few more drops of stannous chloride solution are added, the liquid again boiled, and the test repeated. An excess of hydrochloric acid does not appear to affect the end reaction.

For the estimation of tin, the metal is converted into stannous chloride, then oxidised with an excess of standard ferric chloride solution, and the excess of iron estimated as before with standard stannous chloride. Ordinary ammonium molybdate solution containing nitric acid may be used as indicator if freshly prepared, but after 1—2 weeks it no longer gives the blue colour with stannous chloride. The addition of a drop or two of a phosphate or arsenate, however, restores the property.

J. J. S.

Separation of Nickel and Cobalt. By ARTHUR ROSENHEIM and ERNST HULDSCHINSKY (*Ber.*, 1901, 34, 2050—2057).—The solution containing nickel and cobalt is mixed with an excess of ammonium thiocyanate (12 grams for 50 c.c. of liquid), and then shaken in a Rothe's apparatus with a mixture of amyl alcohol (1 vol.) and ether (25 vols.). The cobalt is removed by the ethereal liquid in the form of a complex thiocyanate (Treadwell, this vol., ii, 284) and the nickel remains in the aqueous liquid; this is evaporated to dryness, carefully ignited, dissolved in dilute nitric acid, and the nickel estimated electrolytically in the presence of ammonium oxalate.

The ethereal solution is shaken with a little dilute sodium hydroxide to remove any iron and then with 15—20 c.c. of 10 per cent. sulphuric acid. The acid cobalt solution is evaporated down, the excess of sulphuric acid driven off, and the cobalt determined electrolytically. The results obtained are remarkably good except when only minute quantities of cobalt are present with large quantities of nickel.

J. J. S.

Separation of Cobalt and Nickel by Electrolysis. By DIMITRI BALACHOWSKY (*Compt. rend.*, 1901, 132, 1492—1495).—On electrolysis at 70—80°, with a current of 0.8 ampere per ND_{100} and an *E.M.F.* of 1 volt, an acetic acid solution of cobalt and nickel containing 3 grams of ammonium thiocyanate, 1 gram of urea, and 1—2 c.c. of ammonium solution for each 0.3 gram of metal, the nickel is deposited

at the cathode in the form of sulphide, the precipitate being complete in one and a-half hours. The sulphide is dissolved in nitric acid, the sulphur removed by filtration, and the metal reprecipitated by electrolysis, either by Classen's method, or in a solution containing ammonium acetate, succinic acid, and carbamide. The cobalt solution is evaporated with nitric acid, the sulphur removed by filtration, and the filtrate electrolysed either by Classen's or the author's method. In the latter process, the solutions are maintained at 70—80°, the current employed being 0·8—1·0 ampere and *E.M.F.* 3·5 volts; the precipitation of cobalt is complete in 3 hours, whilst 4 are required for the deposition of nickel. The results obtained are represented in tabular form.

G. T. M.

Separation of Tungstic and Silicic Acids. By HORACE L. WELLS and F. J. METZGER (*J. Amer. Chem. Soc.*, 1901, 23, 356—358).—Herting (this vol., ii, 284) having stated that the separation of silica from tungstic acid by means of hydrofluoric acid yields erroneous results, the authors have reinvestigated the process and found it to be perfectly trustworthy. The results are the same whether the mixture is evaporated with hydrofluoric acid alone or with the addition of sulphuric acid. The indifferent results obtained by Herting are probably due to the use of the blast, as at a high temperature tungstic acid is sensibly volatile.

L. DE K.

Chemico-toxicological Investigation of Bromoform and of Bromal. By DIOSCORIDE VITALI (*L'Orosi*, 1901, 24, 145—151. Compare Abstr., 1882, 777).—The main portion of this paper has already appeared (this vol., ii, 480). When the quantity of bromoform is very small, it may be detected by burning the hydrogen under a beaker or microscope slide moistened with ammonia, the ammonium bromide thus formed crystallising in dendritic masses.

Bromal may be recognised in the distillate from the acidified material by the addition of ammonium sulphide, with which it gives a red coloration on warming. The liquid may then be mixed with potassium hydroxide and tested for bromoform by any of the methods given above.

For determining the amount of bromoform or bromal present, a known proportion, say two-thirds, of the distillate from the acidified viscera or stomach contents is heated in a reflux apparatus with alcoholic potassium hydroxide for 2 hours, after which the alcohol is driven off, the liquid neutralised, and the alkaline bromide determined either gravimetrically or volumetrically by means of silver nitrate solution.

T. H. P.

Analysis of Commercial Cyanides. Estimation of Cyanic Acid. A peculiar Double Cyanide. Antidote for Cyanides. By OTTO HERTING (*Zeit. angew. Chem.*, 1901, 585—586).—Cyanogen existing as cyanide is best estimated by the process devised by Denigès, and described by Mellor (this vol., ii, 202).

The author describes a new process for the estimation of potassium cyanate. 0·2—0·5 gram of the sample is dissolved in a few c.c. of water, mixed with excess of hydrochloric acid, and evaporated to dryness; the residue contains the nitrogen of the cyanate as ammonia, which is then estimated by distillation with an alkali in the usual

manner. If it is desired to estimate potassium by means of platinum chloride, the residue obtained on evaporating commercial potassium cyanide with hydrochloric acid should be calcined so as to expel ammonium compounds.

The author has met with a peculiar impure compound of potassium and ammonium cyanide in white, amorphous lumps with a strong odour of hydrocyanic acid, and containing 35.85 per cent. of cyanogen, 31.45 per cent. of potassium, and 15.83 per cent. of total nitrogen.

A subcutaneous injection of a 3 per cent. solution of hydrogen peroxide is recommended in cases of poisoning by fumes of hydrocyanic acid.
L. DE K.

Rapid Estimation of Sugar in Beets. By R. S. HILTNER and R. W. THATCHER (*J. Amer. Chem. Soc.*, 1901, 23, 299—318).—The process is based on the fact that beets may be assumed to contain 83 per cent. of water, and that the polariscopic reading is not sensibly affected by the moisture varying a few per cents.

The sample of pulp properly rasped is weighed into a tared capsule, a table is consulted and the required amount of water containing basic lead acetate (about three times the weight of the sample) is added, the capsule is covered with a tightly fitting lid, and the contents thoroughly shaken. The liquid is then filtered and the filtrate polarised.

L. DE K.

A new Sugar Reaction. By T. SOLLMANN (*Chem. Centr.*, 1901, i, 1245; from *Centr. Physiol.*, 25, 34—36).—Ordinary Fehling's solution may be replaced by a cobalt or nickel solution prepared by mixing 10 c.c. of a 1 per cent. solution of cobalt nitrate or nickel sulphate with 50 c.c. each of a 10 per cent. solution of sodium hydroxide and a 5 per cent. solution of sodium potassium tartrate. The nickel solution is apple-green; on boiling with dextrose, it becomes yellow. The cobalt solution is at first colourless; it gradually becomes blue-green, or on boiling sky blue. When boiled with dextrose, its colour passes through emerald green and yellowish-green to reddish-brown. The reaction is $1\frac{1}{2}$ —2 times as sensitive as that with copper. Both reagents give the reaction with dextrose, invert sugar, lactose, galactose, aldehydes, and various gums. Proteids also produce characteristic colour changes, but distinct from those given by sugars. M. J. S.

The Amount of Pentosans in Gum Arabic. By RUDOLF HEFELMANN (*Zeit. öffentl. Chem.*, 1901, 11, 195—198).—A table is given showing the commercial value, percentage of water and ash, and the amount of furfuraldehyde yielded by 1 gram of 24 specimens of gum arabic of different origin and also of cherry-gum. The table also contains the amount of pentosans and araban corresponding with the furfuraldehyde. The estimation of the pentosans is not, as was hoped, of much practical value in detecting an admixture of cherry-gum in gum arabic.

The analytical process followed was that of Tollens and Flint (*Abstr.*, 1896, ii, 580), in which the furfuraldehyde is precipitated with phloroglucinol.
L. DE K.

Estimation of Pentosans. By GEORGE S. FRAPS (*Amer. Chem. J.*, 1901, 25, 501—508).—The method of estimating pentosans in vegetable materials consists in distilling the substance with hydrochloric acid and precipitating the furfuraldehyde in the distillate with phloroglucinol; this distillate may, however, also contain fatty acids, a substance which slowly separates as a black precipitate, and another substance, provisionally termed 'furaloid,' which is destroyed by redistillation; all these compounds may appear in the phloroglucinol precipitate.

The author has proved that the loss which occurs on redistilling the distillate is not due to oxidation, or to decomposition of the furfuraldehyde, and is therefore occasioned by some substance (or substances) which precipitates phloroglucinol and is destroyed, wholly or in part, by a second distillation. This 'furaloid' was determined in a number of vegetable substances by the following process. The material was distilled with hydrochloric acid, the distillate was divided into two portions and one portion redistilled; the loss was assumed to represent the 'furaloid' present. All the materials tested yielded 'furaloid,' the quantity varying from 7 to 23 per cent. The substances which furnish the 'furaloid' are hydrolysed by 1.25 per cent. sulphuric acid, and on evaporation the 'furaloid' is lost. On hydrolysing the excrement of a sheep fed with timothy hay, it was found that the substances which yield the 'furaloid' had disappeared to a greater extent than the pentosans; their digestibility is about 75 per cent. compared with 60 per cent. for that of pentosans. The 'furaloid' is not formed by the action of hydrochloric acid on pentoses. E. G.

Estimation of the True Amount of Starch in Potatoes. By PAUL BEHREND and H. WOLFS (*Zeit. angew. Chem.*, 1901, 461—465).—The method proposed by Baumert and Bode for the estimation of real starch in potatoes (this vol., ii, 44) is strongly recommended.

L. DE K.

A new Starchy Product used for Confitures and Creams. By FREHSE (*Ann. Chim. anal. appl.*, 1901, 6, 210—211).—The author has analysed a mixture used for making blanc manges, &c., and found it to consist of sugar and flavouring matter, with 8.5 per cent. of wheat starch. This starch has been subjected to a special treatment, and, although insoluble in cold water, it readily dissolves in boiling water, forming a transparent jelly on cooling. Its microscopical appearance is not destroyed by boiling for a few minutes, and it is also coloured blue by iodine; its detection is, therefore, an easy matter. L. DE K.

Amount of Volatile Fatty Acids in Dutch Butter. By R. RACINE (*Zeit. angew. Chem.*, 1901, 568—571).—The author agrees with Reicher (this vol., ii, 292) and van Ryn (*Abstr.*, 1899, ii, 822) as to the occasional low Reichert-Meissl figure of undoubtedly genuine Dutch butters. L. DE K.

[**Estimation of Alkaloids in Urine.**] By H. GUILLEMARD (*Compt. rend.*, 1901, 132, 1438—1440).—See this vol., ii, 521.

General and Physical Chemistry.

Refractive Indices of Mixtures of Liquids. By J. DE KOWALSKI and JEAN DE MODZELEWSKI (*Compt. rend.*, 1901, 133, 33—35).—The refractive indices (for yellow sodium light) and densities of various mixtures of alcohol and benzene, alcohol and toluene, and chloroform and ether, have been determined. Gladstone's and Lorenz's formulæ can be equally well used for the calculation of the refractive indices of these mixtures according to the mixture rule.

Philip (Abstr., 1898, ii, 9) found that neither of these formulæ (when \sqrt{k} was substituted for the refractive index) agreed with the results obtained for the dielectric constants of liquid mixtures. According to Drude, the difference between the dielectric constant and the square of the index of refraction for long light waves depends on the absorption of the substance in the ultra-red part of the spectrum. Since the anomalies presented by the dielectric constant are not found for the refractive indices, it is probable that it is only the absorption in the infra-red which changes irregularly in the mixtures studied.

J. McC.

Sensitiveness of Diazo-compounds to Light. By OTTO RUFF and VICTOR STEIN (*Ber.*, 1901, 34, 1668—1684).—See this vol., i, 619.

The Chlorine-Hydrogen Gas Cell. By ERICH MÜLLER (Dresden) (*Zeit. Elektrochem.*, 1901, 7, 750—752).—The author points out that Akunoff (this vol., ii, 81) has made two errors in his calculations. When the figures are correctly calculated, the *E.M.F.* of the hydrogen-chlorine cell is 1.37125—0.0008066 volts, and the heat developed by the reaction 36778 cal.

The quantities of heat evolved by the formation of hydrochloric acid in 3*N* solution from hydrogen and chlorine is 37854 cal., whilst from hydrogen and hypochlorous acid it is 37404 cal.

Since, however, chlorine and hypochlorous acid are in equilibrium in the solution, in accordance with the equation $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HClO}$, it is doubtful whether thermochemical measurements can decide which reaction represents the mechanism of the production of *E.M.F.* in the cell. The result should be the same whichever assumption is made.

T. E.

Theory of the Accumulator. By EMIL ABEL (*Zeit. Elektrochem.*, 1901, 7, 731—733).—By applying the equations previously obtained for the potential difference between a metal and a solution containing its *m*- and *n*-valent ions (this vol., ii, 376), the author shows that Le Blanc's theory of the lead accumulator (the peroxide electrode is in equilibrium with $\text{Pb} \cdots$ ions) explains its behaviour in as simple a manner as Liebenoff's theory (the peroxide electrode is reversible with respect to PbO_2' ions), and that, therefore, there is no reason to give preference to either view.

T. E.

Electrochemical Behaviour of Nickel Ammonium Sulphate. By W. PFANHAUSER (*Zeit. Elektrochem.*, 1901, 7, 698—710).—The equivalent conductivities of solutions of nickel and ammonium sulphates and of the double salt have been determined, and are tabulated in the original.

In the more concentrated solutions, the conductivity of the double salt is less than the sum of the conductivities of the constituents, a result which indicates the formation of a complex ion. This is confirmed by measurements of the transference numbers, which show that the double salt exists in its saturated solution at 18°, mainly in the form of the ions NH_4 and $\text{Ni}(\text{SO}_4)_2$. In more dilute solutions, however, the ions NH_4 , Ni , and SO_4 exist.

Taking the value of the calomel electrode as -0.56 volt, the following *P.D.*'s between metals and normal solutions of nickel sulphate were found :

| Metal. | NiSO_4 . | $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2$. |
|--------------------------------|-------------------|---|
| Nickel | -0.041 volt. | -0.060 volt. |
| Lead..... | -0.005 „ | -0.007 „ |
| Zinc..... | $+0.482$ „ | $+0.493$ „ |
| Copper..... | -0.569 „ | -0.591 „ |
| $\text{Ni}(\text{OH})_2$ | -1.135 „ | -1.152 „ |

In electrolysing solutions of nickel sulphate, or of the double salt, with nickel electrodes, polarisation is observed. The lower value (1.06 volts) corresponds with the decomposition of water and evolution of oxygen at the anode. The higher value (about 2.3 volts in neutral, and 1.9 volts in acid, solutions) is attributed to the formation of nickelic sulphate at the anode, the greater part of which is at once hydrolysed to nickelic hydroxide. Attempts to prepare this salt chemically failed, but a solution of nickelic acetate was obtained by dissolving the hydroxide in cold glacial acetic acid. T. E.

Electrolysis of Fused Salts. By RICHARD LORENZ (*Zeit. Elektrochem.*, 1901, 7, 753—761).—A cell containing fused lead chloride with carbon electrodes, the one dipping into fused lead, the other being saturated with chlorine, behaves like an accumulator. When the electrodes are properly separated from each other, the cell maintains a constant *E.M.F.* of 1.2 volts at 600° for 3 hours, so that there is no doubt as to the real *E.M.F.* of this combination. If the dark grey solution of lead surrounding the cathode of the polarised lead chloride cell passes over to the anode, the *E.M.F.* at once sinks, and only returns to its original value when the fused lead chloride surrounding the anode has become transparent again owing to the conversion of the dissolved lead into lead chloride. Unless great care is taken in separating the anode and cathode liquids, the polarisations observed are always lower than the normal values. This partial depolarisation is accompanied by a disappearance of the products of the electrolysis, so that the lower the polarisation the smaller is the yield. It was found that when a lead chloride cell was polarised for a short time and then allowed to discharge, the polarisation fell very rapidly to a fairly constant value, nearly 0.5 volt below the normal *E.M.F.* After each repetition of the polarisation, however, the discharge *E.M.F.*

remained for a longer time at the normal high value before falling, and then passed through the lower value much more quickly. The cause of this was found by studying the evolution of chlorine at the carbon anode. Especially with a new anode the quantity of chlorine evolved in the early stages of electrolysis is considerably less than equivalent to the quantity of lead deposited; since the fused salt round the anode always has the composition PbCl_2 , the missing chlorine is absorbed by the carbon anode, and it is only when this is saturated that the normal value of the polarisation is reached. The apparently anomalous lower values of the polarisation are all due to partial depolarisation.

In passing, the author states that optical experiments have shown that the dark grey "metallic fogs" observed round the cathode are actually solutions of the metals in the fused salts. T. E.

Electrochemical Behaviour of Acetylene. By ALFRED COEHN (*Zeit. Elektrochem.*, 1901, 7, 681—685).—The discharge potential of oxygen from a solution of potassium hydroxide is depressed, when acetylene is passed through the solution, from about 1.7 to 1.2 volts. The chemical reaction of which this depression is an indication is the oxidation of acetylene to formic acid, which takes place quantitatively when the *E.M.F.* employed lies between the above limits.

In solutions of sulphuric acid, the presence of acetylene diminishes the anodic polarisation by about 0.19 volt. The chemical change in this case is the oxidation of acetaldehyde (formed by the action of acetylene on sulphuric acid) to acetic acid. The current efficiency is 100 per cent. when the *E.M.F.* used is less than that required for the liberation of oxygen.

In acid solutions, acetylene does not act as a depolariser for the halogens except in the presence of a carrier, such as phosphorus tribromide, when a considerable depolarisation occurs. T. E.

Applicability of the Law of Mass Action to Strong Electrolytes. By H. VON STEINWEHR (*Zeit. Elektrochem.*, 1901, 7, 685—687).—When electrolytes are dissolved, contraction occurs; this may be taken to indicate an increase in the internal pressure of the liquid. External pressure affects the degree of dissociation, and it is assumed that internal pressure has an equal effect. The degrees of dissociation of two solutions of the same electrolyte are therefore only comparable when measured at the same total (internal + external) pressure. The effect of pressure is given by the equation $RT(\log K_1 - \log K_2) = (p_1 - p_2)\Delta v$ where K_1 and K_2 are the dissociation constants at pressures p_1 and p_2 and Δv is the corresponding change of volume.

To find the increase of internal pressure due to the dissolution of common salt in water, the author makes use of the fact that the rate of inversion of cane sugar by acetic acid is increased in presence of salt. He assumes that the increase of internal pressure due to the addition of the salt increases the dissociation of the acid, and hence the rate of inversion. Since the influence of pressure on the dissociation of acetic acid is known, the pressure required to produce the observed effect is capable of calculation. The dissociation constants of

sodium chloride calculated for the same pressure in the way indicated are much more nearly constant than the uncorrected numbers.

T. E.

The Theory of Electrolytic Dissociation as viewed in the Light of Facts recently ascertained. By LOUIS KAHLENBERG [with ARTHUR A. KOCH and ROY D. HALL] (*J. Physical Chem.*, 1901, 5, 339—392).—An adverse criticism of Arrhenius' electrolytic dissociation theory and its applications. Cryoscopic and ebullioscopic determinations have been made with a large number of salts in aqueous solution over a wide range of concentration; further, conductivity determinations have been made with the same solutions at 0° and 95°. On the basis of this experimental material, it is maintained that there is no such connection between the freezing points and boiling points of solutions on the one hand, and their electrical conductivity on the other, as is claimed by Arrhenius' theory; in numerous cases, there is not even a qualitative agreement. The author examines a number of problems on which the theory has been brought to bear, and contends that, whilst it has stimulated research on many lines, it is quite inadequate as a key to the phenomena of solution.

J. C. P.

Dissociation of Electrolytes. Chemical Dissociation of Copper Sulphate under the influence of Water and Temperature. By C. HENSGEN (*J. pr. Chem.*, 1901, [ii], 63, 554—562).—It is shown that in a solution of copper sulphate saturated at 4° with crystals of the composition $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, the proportion of $\text{CuO} : \text{SO}_3$ changes; after 3 days it is 1:1.014, and after 8 days 1:1.027. If this saturated solution is diluted, the proportion of copper oxide further decreases. Under certain conditions of dilution and temperature, the proportion $\text{CuO} : \text{SO}_3$ in the solution may become 1:1.454.

The author has observed similar changes to take place also in solutions of zinc, magnesium, and calcium salts.

K. J. P. O.

Model illustrating Measurements of the Mobility and Transference of Ions. By B. D. STEELE (*Zeit. Elektrochem.*, 1901, 7, 729—731).—This model illustrates, not only the transference of the ions of a single salt submitted to electrolysis, but also the movement of the boundary between solutions of two salts possessing a common ion for the case that the slower ion follows the faster. To understand the construction, the diagram is required.

T. E.

Speed of Migration of Ions in dilute Solutions. By HANS JAHN [BERLINER, P. BOGDAN, BUKSCHNEWSKI, GOLDBABER, METELKA, OPPENHEIMER, and REDLICH] (*Zeit. physikal. Chem.*, 1901, 37, 673—712).—From exact determinations of the changes of concentration of dilute solutions in electrolytic cells, the following limiting values for the cationic transport numbers have been obtained: Hydrogen (HCl), 0.826, (HNO_3), 0.830; potassium (KCl), 0.497, (KBr), 0.496; sodium (NaCl , NaBr), 0.396; lithium (LiBr), 0.330; barium (BaCl_2), 0.447; cadmium (CdCl_2 , CdBr_2), 0.432, (CdI_2), 0.443; silver (AgNO_3), 0.471; and copper (CuSO_4), 0.375.

J. McC.

An Electrometric Method to determine the Presence of very small Quantities of Electrolytes whose Ions are transported at different Speeds. By MAX OKER-BLOM (*Zeit. physikal. Chem.*, 1901, 37, 665—672).—Two wide Ostwald normal-electrodes with about 8 sq. cm. mercury surfaces are filled with 0.1 *N* potassium chloride solution. The side tubes dip into the wide ends of two small vessels of 2 c.c. capacity, the other ends of which are drawn out so that the bore is 1 mm. and are turned upward. These small vessels contain solutions of sodium chloride of different concentration (0.1 *N* and 0.00001 *N*), or dilute solutions of potassium chloride (0.00001 *N*), one of which also contains mannitol (1 *N*). A small strip of filter paper (15 mm. long \times 3 mm. broad), which has been boiled with distilled water and thoroughly washed, is moistened with a drop of the solution to be examined, and placed so as to connect the narrow ends of the two small vessels. Poggendorff's condensation method is used to determine the *E.M.F.*, an accumulator being employed for comparison, and the direction of the current is indicated by a Lippmann electrometer. Using sodium chloride solutions of different concentration in the small vessels, it has been found that the *E.M.F.* (0.00001 *N* NaCl \rightarrow 0.1 *N* NaCl) diminishes when the filter paper is moistened with lactic acid or potassium dihydrogen phosphate with decreasing concentration of the electrolyte, and ultimately changes direction. Using potassium chloride solutions (0.00001 *N* and 0.1 *N*) instead of the sodium chloride, a similar diminution of *E.M.F.* has been noticed for decreasing concentrations of these electrolytes and hydrochloric acid.

The fact that a current is obtained when the potassium chloride solutions in the small vessels (0.00001 *N* KCl in one, and 0.00001 *N* KCl and 1.0 *N* mannitol in the other) are connected with the filter paper moistened with the solution of the electrolyte (when directly connected there is no current), coupled with the fact that here too the *E.M.F.* diminishes with decreasing concentration of the electrolyte, leads the author to explain the phenomenon as due to the rates of migration of the cation and anion into the two solutions of different viscosity.

J. McC.

Cryoscopic Experiments with Methylene Iodide. By FELICE GARELLI and VITTORIO BASSANI (*Gazzetta*, 1901, 31, i, 407—416).—Methylene iodide is a very difficult substance to use as a cryoscopic solvent as it crystallises with extraordinary slowness, so that the thermometric column only very gradually attains the freezing temperature, and it is with great difficulty, and by taking many precautions, that concordant readings can be obtained. The readings made even with the solvent alone oscillate about two points, differing by about 0.4°, as if the liquid possesses two distinct freezing temperatures. From measurements with ethylene dibromide, benzene, and iodine, the molecular depression of the freezing point of methylene iodide is found to be roughly 140. Stannic iodide, arsenic tri-iodide, and mercuric iodide have normal molecular weights in this solvent, and sulphur gives a value corresponding with the molecule S_8 . A

sample of not quite pure antimony tri-iodide gave a molecular weight varying from 380.3 to 457.8 instead of to 499.22. T. H. P.

A new Manometer, and the Law of Gas Pressure between 1.5 and 0.01 mm. of Mercury. By LORD RAYLEIGH (*Trans. Roy. Soc.*, 1901, 196, 205—223; and *Zeit. physikal. Chem.*, 1901, 37, 713—734).—An extremely exact measurement of gas pressure can be made with the manometer described, in which a mercury surface is caused to approach a glass point, and the motion necessary to bring about coincidence of the point and its image is measured by a mirror and scale method. At the highest pressure (1.5 mm.) the error may be about 0.001 mm., and at the lowest pressure it amounts only to 0.0004 mm. Using this instrument in the investigation, it has been proved that Boyle's law applies rigorously to nitrogen (containing 1 per cent. of argon), hydrogen, and oxygen within the range of pressure from 1.5 to 0.01 mm.

The anomaly found by Bohr (*Ann. Phys. Chem.*, 1886, [ii], 27, 479) for oxygen, although carefully sought for, could not be confirmed.

J. McC.

Chemical Reactions in Dissolved or Gaseous Systems: Vapour Tension: Avogadro's Hypothesis. By A. PONSOT (*Compt. rend.*, 1901, 132, 1551—1553. Compare Abstr., 1900, ii, 337, 392).—A theoretical paper, in which it is shown that if the solvent takes no part in the reaction, the formation of a system which is the only one capable of existence at infinite dilution, and which decreases as the solvent is abstracted, diminishes the vapour tension of the solvent. The formation of the opposed system, on the other hand, increases this tension. If V_1 is the volume of the solution when system I alone is present, V_2 that when only system II is formed (II being that system which increases with decreasing external pressure) then $\pi(V_2 - V_1)$ must be positive, no matter what value π (the osmotic pressure) has. In a gaseous system $P(V_2 - V_1)$ is positive, P being the pressure exerted on the gas.

If we consider the equilibrium represented by $n_1A + n_2B \rightleftharpoons n_3M + n_4N$, then when only one system is present $PV_1 = n_1p_1v_1 + n_2p_2v_2$ and $PV_2 = n_3p_3v_3 + n_4p_4v_4$ (v being the molecular volume); but $pv = iRT$, therefore (since $V_2 - V_1$ is positive) $i_3n_3 + i_4n_4 > i_1n_1 + i_2n_2$. In limited chemical reactions, the equilibrium of which varies with temperature and pressure, if $n_3 + n_4 = n_1 + n_2$ or if $n_1 = n_2 = n_3 = n_4$, then the values of i must be unequal, which proves that Avogadro's hypothesis is not rigorously exact. The same conclusion may be drawn with regard to solutions.

J. McC.

Gay-Lussac's Law and the Dissociation of Gaseous Compounds. By A. PONSOT (*Compt. rend.*, 1901, 132, 1401—1404).—A mathematical paper in which the author shows that dV/dm (coefficient of increase of volume on account of dissociation) must be positive. This has hitherto been regarded as doubtful, but it is shown to be a consequence of the accepted result that $\delta m/\delta T$ is positive. When the equilibrium between a gaseous substance and its products of dissocia-

tion is dependent on the pressure, it must also be dependent on the temperature, and variation of either of these will disturb the equilibrium. When the volume or temperature increases indefinitely, the dissociation tends to become complete. Since dV/dm_{PT} is always positive, it follows that the volume of a dissociable gaseous compound is smaller than the volume of the mixture of its dissociation products.
J. McC.

Preparation of Osmotic Membranes by Electrolysis. By HARMON N. MORSE and D. W. HORN (*Amer. Chem. J.*, 1901, 26, 80—86).—A semipermeable membrane may be deposited in the wall of a porous cell by the following electrolytic method. The air is first removed from the wall by putting a solution of potassium sulphate containing 0.5 gram per litre in the cup and the beaker in which it is placed, and passing a current between the electrodes in the direction of the one within the cup; the water in passing through the wall effectively sweeps out the air. The cup is then left in distilled water until required. In order to form the membrane, the wet cup is placed in a beaker and surrounded with an electrode of sheet copper, the electrode within the cup being of platinum; a solution of copper sulphate ($N/10$ or $N/5$) is placed outside, and a solution of potassium ferrocyanide (also $N/10$ or $N/5$) inside the cup, and on passing the current a semipermeable membrane is formed in the wall midway between the two surfaces. A number of experiments made to test the strength of the membranes showed that they are able to withstand a pressure of 4.5 atmospheres.
E. G.

Capillary Constants of Organic Liquids. By PHILIPPE A. GUYE and ACHILLE BAUD (*Compt. rend.*, 1901, 132, 1553—1555. Compare this vol., ii, 437).—An examination of some oximes and urethanes shows that all of these are polymerised in the liquid state. Of the aliphatic urethanes, the methyl derivative is less polymerised than the ethyl, which, in turn, is simpler than the isopropyl compound.

The results so far obtained indicate that polymerisation in the liquid state is associated with the presence of certain groups: OH (alcoholic), OH (acidic), CO (ketones and aldehydes), CN (nitriles), and NH_2 (aromatic amines). Compounds containing two of these groups are more polymerised than those of the same molecular complexity containing only one.

The view is expressed that the polymerisation of liquids as revealed by the capillarity and other physical properties is more of the nature of a chemical phenomenon, analogous to the polymerisation of aldehyde to paraldehyde, or cyanogen to tricyanogen, and is quite different from a physical association of simple chemical molecules.
J. McC.

Resorption of one Solution by another. By MAX OKER-BLOM (*Zeit. physikal. Chem.*, 1901, 37, 744—750).—A copper ferrocyanide film on an insoluble gelatin membrane closes a glass tube of 10 mm. bore. Three c.c. of copper sulphate solution are put into the tube, into which a narrow tube is then tightly fitted, so that the liquid rises about 60 mm. The cell is then placed in a solution of sodium chloride. The film is permeable by water and by [the ions of] sodium chloride,

but does not allow copper sulphate to pass. A normal solution of sodium chloride was used, and various solutions of copper sulphate, the most concentrated of which was 0.5 *N*. The column of liquid in the narrow tube at first falls, since the osmotic pressure of the sodium chloride is greater than that of the copper sulphate. After some time, which depends upon the initial concentration of the copper sulphate, the column reaches a minimum, and then rises to a height which may be considerably greater than it was initially. When the meniscus of the column has reached its lowest point, the two solutions are isotonic, and this has been attained by (1) passage of water from the inside to the outside, whereby the concentration of the copper sulphate has increased and that of the sodium chloride has diminished, and (2) passage of sodium chloride through the film, whereby the molecular concentrations of the two solutions tend to become equal. The succeeding rise of the column is explained by the fact that the sodium chloride tends to distribute itself evenly throughout the combined solution, and as the copper sulphate is prevented from doing so by the film, the molecular concentration of the inner solution becomes greater than that outside the cell, that is, the osmotic pressure is greater inside than outside. The lowest concentration of copper sulphate which is still able to exhibit resorption towards a normal sodium chloride solution has not yet been ascertained.

J. McC.

Physical Properties of Albuminous Micelles. By SWIGEL POSTERNAK (*Ann. Inst. Pasteur*, 1901, 15, 169—208 and 451—496. Compare this vol., ii, 231).—A *résumé* of the properties of colloidal solutions and a comparison of the properties of micelles. The following are the more important conclusions drawn from theoretical considerations and numerous experimental data. The albuminous micelle has a constant elasticity and a variable size, which is increased by heat and decreased by the presence of free ions; the solubility of a colloid is occasioned by the size of the micelles being diminished by an electrical charge from free ions. The author takes the view that the different characters of colloidal micelles are the manifestations of an "adhesive affinity," and that in the precipitation of a colloid by mineral matters the latter must necessarily be present in the precipitate. R. H. P.

Velocity of Reaction before complete Equilibrium and before the Point of Transition, &c. Part I. By MEYER WILDERMAN (*Phil. Mag.*, 1901, [vi], 2, 50—92. Compare Abstr., 1900, ii, 200).—The paper is largely mathematical and unsuitable for abstraction. A method is described by which the velocities of ice separation, ice melting, and the separation of salts from supersaturated solutions have been investigated. All these reactions are regulated by one and the same general law, as expressed by the equation $dt/dT = K'(t_0 - t)(t - t_{0v} + K)$, where t_0 is the temperature of equilibrium, and t_{0v} is the temperature at which crystallisation is started.

J. C. P.

Reciprocal Influence of Two Catalytic Reactions in the same Medium. By ANGELO COPPADORO (*Gazzetta*, 1901, 31, i, 425—450).—The author has studied the mutual influence which the inversion of sucrose by acids and the hydrolysis of methyl acetate by

acids exert on one another when the two reactions take place in the same medium. The results obtained are given shortly in the following tables, which show the reaction constants obtained under different conditions:

Inversion of sucrose.

| Concentration of acid | <i>N</i> /2·5 | <i>N</i> /12·5 | <i>N</i> /25 |
|---|---------------|----------------|--------------|
| „ sucrose | 8 per cent. | 16 per cent. | 16 per cent. |
| Temperature | 25° | 40° | 40° |
| HCl { Without methyl acetate.... | 19·83 | 63·05 | 16·87 |
| With 1 c.c. „ „ | 19·68 | 57·69 | 13·77 |
| With 2 c.c. „ „ | — | 49·81 | 12·74 |
| H ₂ SO ₄ { Without methyl acetate.. | — | 32·98 | 9·11 |
| With 1 c.c. „ „ | — | 23·49 | 8·60 |
| With 2 c.c. „ „ | — | 20·90 | 8·37 |

Hydrolysis of methyl acetate.

| Concentration of acid | <i>N</i> /2·1 | <i>N</i> /12·5 | <i>N</i> /12·5 | <i>N</i> /25 | <i>N</i> /25 |
|--|---------------|----------------|----------------|--------------|--------------|
| „ methyl acetate | 1 c.c. | 1 c.c. | 2 c.c. | 1 c.c. | 2 c.c. |
| Temperature | 25° | 40° | 40° | 40° | 40° |
| HCl { Without sucrose..... | 16·54 | 9·13 | 9·85 | 4·70 | 5·01 |
| With „ | 16·25 | 10·25 | 11·77 | 5·42 | 5·74 |
| H ₂ SO ₄ { Without „ | — | 5·78 | 6·47 | 3·23 | 3·39 |
| With „ | — | 6·47 | 7·49 | 3·66 | 3·89 |

The velocity of inversion of sucrose is hence diminished by the presence of methyl acetate, and the author considers such diminution to be due entirely to the modification produced in the medium by the addition of methyl acetate, and not to the hydrolysis of the latter. The increase brought about in the rate of hydrolysis of methyl acetate when sugar is present in the liquid is shown by the author to be caused by the increase of the ratio of acid to water, due to the replacement of some of the water by sucrose; when the influence of the volume occupied by the sugar is removed by keeping the quantity of water constant and adding the sugar after the mixture of acid and methyl acetate is made up to volume, the reaction constant is found to be the same when sugar is present as when it is not. The inversion of the sucrose hence exerts no influence on the velocity of hydrolysis of methyl acetate. This conclusion is confirmed by the observation that the sucrose may be replaced by a corresponding quantity of invert sugar without altering the velocity of hydrolysis of methyl acetate.

T. H. P.

Experimental Verification of a Law of Chemical Mechanics. By H. PÉLABON (*Compt. rend.*, 1901, 132, 1411—1413).—The reaction $\text{HgS} + \text{H}_2 \rightleftharpoons \text{H}_2\text{S} + \text{Hg}$ has been studied by the action of hydrogen on mercury sulphide (with and without excess of mercury), and by the action of hydrogen sulphide on mercury. The four components of the system are volatile, and the results obtained show that $p_1 p_2 / p_3 p_4 = f(T)$, where $p_{(1,2,3,4)}$ are the partial pressures of mercury sulphide, hydrogen, hydrogen sulphide, and mercury respectively.

J. McC.

Comparative Crystallographical Study of the Double Selenates of the Series $R_2M(SeO_4)_2 \cdot 6H_2O$.—Salts in which M is Magnesium. By ALFRED E. TUTTON (*Proc. Roy. Soc.*, 1901, 68, 322—323).—The conclusions reached in the present paper are generally similar to those arrived at from a study of the zinc group (see Abstr., 1900, ii, 593); R represents one of the metals potassium, rubidium, and caesium, and there is a uniform progression in properties parallel to the increase of atomic weight. The progressive diminution of double refraction, however, according to a rule already established, leads in the case of caesium magnesium selenate to such close approximation of the three refractive indices that the crystals of this salt exhibit peculiar optical phenomena. J. C. P.

Study of Growing Crystals by Instantaneous Photomicrography. By THEODORE W. RICHARDS and EBENEZER HENRY ARCHIBALD (*Amer. Chem. J.*, 1901, 26, 61—74).—It has been suggested by several observers that the formation of crystals is preceded by that of minute globules, which rapidly unite and assume the crystalline form. In order to study this point, the authors have taken a series of successive instantaneous photomicrographs of crystals of sodium nitrate, barium chloride, copper sulphate, and ferrous ammonium sulphate at the moment of their formation. An enlargement of more than 4000 diameters was obtained, and both ordinary and polarised light were used, but in no case was the production of globules detected. It was found that the growth of the crystal is much more rapid during the first second of its formation than at any subsequent period.

The apparatus employed is described with the aid of a diagram, and some of the photographs are reproduced. E. G.

Modification of Kipp's Apparatus. By F. C. THIELE (*Chem. Zeit.*, 1901, 25, 468).—The top bulb of the "Kipp" is furnished at the bottom with a perforated cork, through which passes a tube reaching upwards to two-thirds of the height of the bulb. The top is fitted with a doubly perforated cork through which passes the usual safety funnel and also an overflow tube reaching nearly to the bottom of the bulb; this tube is connected at the external end with an india-rubber tube furnished in the centre with a screw clamp and connected at the other end with a glass tube, which is in turn connected with a tube bent at an angle of 120° passing through an indiarubber cork down to the bottom of the lower bulb. The central bulb contains the gas-generating mass, and is provided with the usual gas exit tube.

When the apparatus is wanted for use, the top cork is removed and the bulb half filled with acid. After inserting the cork, the screw clamp and the exit tube are opened, and by blowing into the safety funnel, the bent tube is filled with acid. Acid is now poured through the funnel until the lower bulb is nearly full. The apparatus is now closed, and the top bulb filled about one-third with acid. If now the gas tap is opened first, and then the screw clamp, the acid rises rapidly in the central bulb and action sets in; the current is then easily regulated by means of the gas tap. When not in use, the screw clamp is closed first and then the tap; the excess of acid

at once ascends into the top bulb without being able to run back. When the apparatus wants emptying, it is only necessary to remove the glass tube connecting the two pieces of india-rubber, and the screw clamp is opened; the top and bottom bulbs are then speedily emptied. The overflow tube may also be replaced by an open glass tube sealed to the lower bulb; this does away with the blowing through the safety funnel, and the acid circulates automatically.

L. DE K.

Lecture Experiments to Demonstrate the Principle of Conservation of Weight. By ROBERTO SALVADORI (*Gazzetta*, 1901, 31, i, 400—401 and 474—476).—The experiments given by Ostwald (*Grundlinien der anorganischen Chemie*, 1900) to illustrate the conservation of weight during chemical reactions would be more convincing if they were accompanied by an apparent diminution or increase in the quantity of matter taking part in them. The author therefore proposes as lecture experiments: (1) the burning of a piece of phosphorus in a sealed hard glass tube drawn out to a fine point at one end; the tube is weighed before and after burning the phosphorus, the diminution in volume being shown by breaking off the point of the tube under mercury which rises in the tube; (2) in a similar tube, a little concentrated nitric acid and powdered copper are placed out of contact, and the tube sealed and weighed, after which the metal and acid are mixed; when the reaction ceases and the tube cools, it is weighed again to show that no change has occurred, and the point of the tube fused in a flame, when a large volume of red vapours is emitted. Another striking experiment consists in charging one limb of a Λ -shaped tube with sodium amalgam, and the other with saturated aqueous ammonium chloride, sealing the tube, weighing, and then mixing the contents of the two limbs. The tube is rapidly filled with a metallic looking mass of ammonium amalgam, and its weight is found to be unchanged at the end of the reaction.

T. H. P.

Lecture Experiments. By MAXIMILIAN ROSENFELD (*Chem. Zeit.*, 1901, 25, 421—422).—I. Volumetric composition of the air. Iron filings are placed in a small wire-gauze basket attached to a glass rod which passes through the rubber stopper of a gas cylinder. The iron filings are first strongly heated, and then the rubber stopper introduced into the cylinder, which is graduated and placed over water. The iron is slowly shaken out of the basket, and when cold it is observed that one-fifth of the air has been absorbed.

II. Synthesis of sodium or potassium bromide. The metal is ground up with about 10 times its weight of sodium chloride or potassium bromide, and the powder thus obtained thrown into bromine vapour and well shaken until the colour of the bromine has disappeared. Sodium chloride may be synthesised by a similar method.

J. J. S.

Inorganic Chemistry.

Hydrogen Peroxide. By ARTHUR MARCUSE and RICHARD WOLFENSTEIN (*Ber.*, 1901, 34, 2430—2432).—See this vol., i, 608.

Oxides of Chlorine. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1901, [iii], 25, 659—665).—A 0.5—0.7 per cent. solution of chlorine peroxide can be prepared by allowing a dish containing potassium chlorate and slightly diluted sulphuric acid to float on water contained in a larger dish for a couple of hours, the whole being covered by a bell-jar.

On mixing solutions of equivalent quantities of chlorine peroxide and potassium hydroxide, the yellow colour of the peroxide slowly disappears; at the same time, the oxidising power (as estimated by titration with *N*/10 thiosulphate of the iodine set free from hydriodic acid) decreases, until it becomes constant; when the yellow colour is no longer visible. The reaction is thus represented: $2\text{ClO}_2 + 2\text{KOH} = \text{KClO}_2 + \text{KClO}_3 + \text{H}_2\text{O}$; a small amount of chlorine is liberated, which reacts with potassium hydroxide in the usual manner. When a large excess of potassium hydroxide is used, the yellow colour disappears and the titre becomes constant far more rapidly.

When solutions of chlorine peroxide and sodium peroxide are mixed, the yellow colour of the former immediately becomes fainter, and disappears as soon as a sufficient quantity of the latter has been added; at the same time, oxygen is evolved. The faintly alkaline colourless solution thus obtained is without action on indigo or iodised starch-paper, and becomes yellow on addition of acid. After acidification with acetic acid, it gives, with lead nitrate, a precipitate of the characteristic lead chlorite. Estimations of the oxygen evolved, and of the oxidising power of the solution, show that the reaction is represented by the equation: $2\text{ClO}_2 + \text{Na}_2\text{O}_2 = 2\text{NaClO}_2 + \text{O}_2$.

The author finds that the halogens react with solutions of sodium peroxide (containing sodium hydroxide), forming sodium haloid and oxygen; thus with iodine: $\text{Na}_2\text{O}_2 + \text{I}_2 = 2\text{NaI} + \text{O}_2$; at the same time, the sodium hydroxide forms hypoiodite and iodide. K. J. P. O.

Chlorine Peroxide as a Steriliser of Drinking Waters. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1901, [iii], 25, 665—669).—The author points out that the coke employed by A. Bergé (*Mem. Soc. ingénieurs civils de France*, 1900) to remove excess of chlorine peroxide from water which has been sterilised by means of it, has not this effect. To water from an artesian well, containing much calcium and magnesium hydrogen carbonates, a known quantity of chlorine peroxide was added; the titre with thiosulphate slowly decreased, owing to the reaction of the chlorine peroxide with the hydrogen carbonates to form chlorite and chlorate (compare previous abstract). Treatment with coke did not destroy the peroxide, but hastened the formation of chlorite and chlorate. Using small quantities of chlorine peroxide, after treatment with coke, the reaction of the peroxide with

neutral potassium iodide was not given; on acidification, the reaction of chlorite was very marked. With larger quantities of chlorine peroxide, after 3 hours' treatment with coke, a reaction was still given with neutral iodide.

K. J. P. O.

Mechanism of the Reaction on Oxidation by Gaseous Oxygen. By WILHELM MANCHOT and JOHANNES HERZOG (*Zeit. anorg. Chem.*, 1901, 27, 397—419. Compare Abstr., 1900, ii, 546).—I. The oxidation of cobaltous cyanide. The rate of absorption of gas was determined when a solution of cobaltous cyanide was shaken at constant temperature with oxygen. Assuming that the reaction is one of the first order, a satisfactory constant is obtained; towards the end of the reaction, however, a diminution of the constant is observed, and this is attributed to the disturbing effect of the hydrogen peroxide formed. The reaction is bimolecular, and what is measured is the rate of decomposition of water by cobaltous cyanide on the assumption that the atomic oxygen is at once converted into hydrogen peroxide. The oxygen is not absorbed with formation of cobalt superoxide, for then the reaction would necessarily be termolecular.

II. The oxidation of ferrous oxide. Similar observations with solutions of ferrous oxalate, tartrate, and citrate led to irregularities in the constants for the expression of a reaction either of the first or of the second order, but it was found that during the oxidation some oxygen was made active. Results obtained when arsenious acid was added to the solution to take up the active oxygen show that the reaction is of the first order, as a satisfactory constant was found. In auto-oxidation with ferrous oxide, no hydrogen peroxide is produced, and the simplicity of the reaction is not in agreement with the views of van't Hoff, Engler, and Haber on this process.

J. McC.

Formation of Active Oxygen by Ferrous Oxide. By WILHELM MANCHOT [with F. GLASER] (*Zeit. anorg. Chem.*, 1901, 27, 420—431. Compare Abstr., 1900, i, 300).—In order to ascertain the proportion of active oxygen produced to oxygen used in the oxidation of ferrous salts, experiments were made in which large quantities of arsenious acid were used (see preceding abstract). To avoid the direct oxidation of the arsenious acid, potassium carbonate was added to the solution, and it was found that the volume of oxygen absorbed was almost exactly equivalent to 1 atom per molecule of ferrous oxide present. This indicates that the ratio of oxygen used in oxidising to that made active is 1 : 1, and as no hydrogen peroxide is formed, it is probable that in the first place a superoxide, FeO_2 , is produced. By the oxidation of chromous salts with free oxygen, part of the gas is also made active. Experiments with manganese salts are in progress.

J. McC.

Hydrate of Sulphuryl Chloride and its Solution in Water without Change. By GIACOMO CARRARA (*Gazzetta*, 1901, 31, i, 450—452).—Replying to Baeyer and Villiger's criticisms (*Ber.*, 1901, 34, 736; this vol., ii, 311) on the work of Carrara and Zappellari (Abstr., 1894, ii, 412) on the velocity of decomposition of sulphuryl chloride by water, the author points out that in the condi-

tions under which the measurements were made, it is impossible for a hydrate of the chloride to be formed. The author considers that Baeyer and Villiger's work does not prove that sulphuryl chloride dissolves in water without at first undergoing some change.

T. H. P.

Studies on the Solubilities of Salts. VII. Telluric Acid and Allotelluric Acid. By FRANZ MYLIUS (*Ber.*, 1901, 34, 2208—2220).—Concentrated solutions of telluric acid, when super-saturated with sodium hydroxide, yield the salt, $\text{Na}_4\text{TeO}_5 \cdot 8\text{H}_2\text{O}$, which crystallises in slender, felted needles, and is hydrolysed by water to the salt $\text{Na}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$. A corresponding *lithium* salt was also obtained. The solubility curves of the two hydrates $\text{H}_2\text{TeO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ intersect at $+10^\circ$, the dihydrate being stable at higher temperatures. When ordinary telluric acid, $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$, is heated at 140° , it is converted into *allotelluric acid*, probably $(\text{H}_2\text{TeO}_4)_n$, which has a conductivity five times as great as telluric acid, and differs from it in giving white precipitates with solutions of guanidine carbonate and albumin; in aqueous solution, it is only slowly reconverted into telluric acid.

It is noted that extremely small quantities of telluric acid (less than 1 mg.), when taken internally, give to the breath a most offensive odour, probably due to the formation of tellurium methyl.

R. H. P.

Synthetical Formation of Ammonia. By E. BAUR (*Ber.*, 1901, 34, 2385—2391).—In the electrolysis of Divers' solution, that is, a solution of ammonia in a saturated solution of ammonium nitrate, nitrogen is evolved at the anode, and hydrogen at the cathode, in the proportion 1 : 3 by volume. The reaction by which the nitrogen is formed is expressed by the equation, $3\text{NO}_3 + 4\text{NH}_3 = \text{N} + 3\text{NH}_4\text{NO}_3$, whilst the hydrogen is formed by the decomposition, $\text{NH}_4 = \text{NH}_3 + \text{H}$.

When a galvanic element is constructed, using these two gases over Divers' solution, a current is obtained with an *E.M.F.* of about 0.6 volt, and the hydrogen and nitrogen respectively disappear from the positive and negative poles in the proportion of 3 : 1 by volume. A constant *E.M.F.* could only be obtained at -10° . When a 25 per cent. solution of ammonia in *N* potassium chloride was employed, no constant *E.M.F.* was observed.

When, however, the back *E.M.F.*, set up in the electrolysis of solutions of ammonia either in Divers' solution or in *N* potassium chloride was measured, constant values were found.

By the equation $E = E_0 + (RT/n\epsilon_0)\log\pi_0/\pi$, where E_0 = the observed *E.M.F.* at $-10^\circ = 0.59$ volt, and π_0 and π are respectively the vapour pressures of (liquid) ammonia and Divers' solution at temp. T , the value of the *E.M.F.* can be calculated for various temperatures; at 0° $E = 0.604$ volt, and at 15° , 0.627 volt. From the heat of formation of (liquid) ammonia at -10° , which equals 171.1 K , the temperature coefficient of the *E.M.F.* can be calculated, and is equal to 0.00125.

Failure attended all attempts to synthesise ammonia by passing nitrogen and hydrogen over platinum black at 100° , or over chromium

or molybdenum nitride, or by leaving the two gases over platinised platinum foil in the presence of hydrochloric acid. K. J. P. O.

Hydroxylamine Hydriodide. By RICHARD WOLFFENSTEIN and FRIEDRICH GROLL (*Ber.*, 1901, 34, 2417—2420).—The normal *hydriodide*, $\text{NH}_2\text{OH}\cdot\text{HI}$, which Dunstan and Goulding (*Trans.*, 1896, 69, 839) failed to prepare, is obtained by mixing molecular quantities of hydroxylamine and hydriodic acid in aqueous solution and evaporating in a vacuum, initially at 26° , and finally, to complete dryness, over phosphoric oxide at the ordinary temperature. It forms flat, colourless needles, is very hygroscopic, and decomposes explosively at $83\text{--}84^\circ$; it crystallises well from methyl alcohol.

The need is emphasised for greater caution in distilling hydroxylamine, owing to the frequent occurrence of dangerous explosions.

W. A. D.

Preparation of Phosphorus Oxychloride. By FRITZ ULLMANN and A. FORNARO (*Ber.*, 1901, 34, 2172—2173).—Directions are given for the preparation of phosphorus oxychloride by the oxidation of the trichloride with potassium chlorate. To avoid the formation of oxides of chlorine, the chlorate must be quite dry, and should be covered by a little previously obtained oxychloride before the trichloride is gradually added; under these conditions, the formation of the oxychloride proceeds quietly.

R. H. P.

Chemical Equilibria. Phosphoric Acid and Chlorides of the Alkaline Earths. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 133, 5—20).—The author has investigated the acidity or alkalinity, to methyl-orange and phenolphthalein respectively, of mixtures of phosphoric acid or hydrogen phosphates with various proportions of chlorides of the alkaline earths, with and without various proportions of sodium hydroxide. Complete neutrality is rarely obtained with the exact proportions of the reacting substances corresponding with simple equations. In some instances, the establishment of equilibrium requires time, whilst, in others, the result depends on the length of time during which the precipitated phosphate and the liquid remain in contact. The quantity of alkaline earth required to neutralise 1 mol. of phosphoric acid varies from 2 to 4 equivalents, according to the conditions. Minute details of the various experiments are given.

C. H. B.

Studies of the Acids of Phosphorus. I. Velocity of Hydration of Metaphosphoric Acid. By CLEMENTE MONTEMARINI and U. EGIDI (*Gazzetta*, 1901, 31, i, 394—400).—The authors have measured the velocity of transformation of meta- into ortho-phosphoric acid in solutions of different concentrations at a temperature of $23\text{--}25^\circ$. The reaction, represented by the equation $\text{HPO}_3 + \text{H}_2\text{O} = \text{H}_3\text{PO}_4$ should be of the second order, but in dilute solutions the mass of water may be taken as constant, and the reaction as being of the first order. The results show that the velocity constant increases with the concentration of the solution employed, a fact which indicates that the ionic hydrogen present exercises a catalytic action on the reaction. Solutions of metaphosphoric acid hence keep better the more dilute and the more free from other acids they are. T. H. P.

Acidimetry of Arsenic Acid. By A. ASTRUC and J. TARBURIECH (*Compt. rend.*, 1901, 133, 36—38).—Arsenic acid, with methyl-orange as indicator, is monobasic to alkalis and alkaline earths at the ordinary temperature or in hot solutions. With phenolphthalein at the ordinary temperature, it is dibasic, but in hot solutions the colour change takes place after the addition of only $1\frac{1}{2}$ equivalents of an alkaline earth.

If in presence of a chloride of an alkaline earth metal excess of an alkali hydroxide is added to arsenic acid, a tribasic arsenate is precipitated, but if an acid is added until the liquid is neutral to phenolphthalein, this precipitate dissolves, and a dibasic arsenate is formed. If, however, the liquid is boiled, the first precipitate becomes crystalline, and afterwards does not dissolve when the liquid is neutralised. In this respect, arsenic acid behaves differently from phosphoric acid.

C. H. B.

Preparation of Thio-oxyarsenates. By WILLIAM HENRY McLAUCHLAN (*Ber.*, 1901, 34, 2166—2172).—Ammonium thio-oxyarsenate, $(\text{NH}_4)_3\text{AsO}_3\text{S}\cdot 4\text{H}_2\text{O}$, and ammonium hydrogen thio-oxyarsenate, $(\text{NH}_4)_2\text{HAsO}_3\text{S}$, are obtained by the fractional precipitation by alcohol of an ammoniacal solution of a fused mixture of equal parts of arsenious trioxide and sulphur. The author has repeated the work of McCay (this vol., ii, 95), and of Weinland and Lehmann (this vol., ii, 313), and confirms McCay's interpretation of the results.

R. H. P.

Vitrified Quartz. By WILLIAM A. SHENSTONE (*Proc. Roy. Inst.*, 1901, Reprint).—When fragments of quartz, previously heated to 1000° , are thrown into cold water, a white, enamel-like product is obtained, which may be suddenly put into the hottest part of an oxy-hydrogen flame without splintering. Thus the fragments of silica may be fused together into rods, and from the latter tubes and vessels may be constructed. The vitrified silica is harder than felspar, but less hard than chalcedony; its density and refractive index are less than those of quartz. In transparency to ultraviolet rays, vitreous silica is superior to glass, and practically equal to air. Its rate of expansion is extremely small, and this explains its stability when exposed to sudden changes of temperature. Its high melting point should render it serviceable in thermometry and in investigations at high temperatures. Thus it has been shown that nitric peroxide is produced simply by heating a mixture of nitrogen and oxygen in tubes of silica to 1000° . Vitrified silica is, like platinum, slightly permeable to hydrogen at 1000° , and is attacked by hot basic oxides.

J. C. P.

An Acid Triple Salt. By WILHELM MEYERHOFFER and F. G. COTTRELL (*Zeit. anorg. Chem.*, 1901, 27, 442—444).—The salt, $\text{KHMg}(\text{SO}_4)_2 + 2\text{H}_2\text{O}$, is obtained by dissolving leonite, $(\text{MgSO}_4\cdot\text{K}_2\text{SO}_4\cdot 4\text{H}_2\text{O})$,

in 85 per cent. nitric acid and allowing the mixture to crystallise. It separates in prismatic, double-refracting crystals, and when treated with water is converted into picromerite, $\text{MgSO}_4\cdot\text{K}_2\text{SO}_4 + 6\text{H}_2\text{O}$.

E. C. R.

Magnesium Aluminate. By ÉMILE DUFAU (*Bull. Soc. Chim.*, 1901, [iii], 25, 669—670).—Magnesium aluminate, spinel, MgAl_2O_4 , can be easily prepared by heating a mixture of alumina and magnesia in an electric furnace for a few minutes. The powdered mass is extracted with hot nitric acid, which leaves a mixture of carbon and the aluminate, the latter as colourless crystals. Separation is effected by projecting the mixture into methylene iodide. The aluminate, thus prepared, forms colourless octahedra, with a sp. gr. 3.57 at 15°, and is fusible only in the electric furnace. It is slowly attacked by hydrofluoric, hydrochloric, or sulphuric, but not by nitric, acid. Fluorine is without action at the ordinary temperature, but acts on it when heated. Chlorine, bromine, and iodine have no action, whilst sulphur only slowly acts at the temperature of molten glass. Carbon does not reduce the aluminate, but fused alkalis dissolve it easily.

One or two per cent. of coloured oxides give to the aluminate the colours of the different varieties of spinel. No other magnesium aluminate could be obtained by varying the proportion of magnesia and alumina.

K. J. P. O.

Cadmium Suboxide. By SIMEON M. TANATAR (*Zeit. anorg. Chem.*, 1901, 27, 432—436).—*Cadmium suboxide*, Cd_4O , is obtained more easily than lead suboxide (this vol., ii, 451) by cautiously heating cadmium oxalate in a current of dry carbon dioxide. It is a green, amorphous powder, decomposes when treated with acids or ammonia into cadmium oxide and metallic cadmium, is slowly decomposed by water, and is stable in dry air; its sp. gr. is 8.177 to 8.207 at 19°.

When the suboxide is heated to the melting point of cadmium in a current of carbon dioxide, it is converted into a yellowish-brown powder which is a mixture of metallic cadmium and cadmium oxide.

E. C. R.

Bismuth Suboxide. By SIMEON M. TANATAR (*Zeit. anorg. Chem.*, 1901, 27, 437—441).—*Bismuth suboxide*, BiO , is easily obtained by heating the oxalate, $\text{Bi}_2\text{O}_3(\text{C}_2\text{O}_4)_2$, in a current of carbon dioxide. It is a black powder, stable in the air, is slowly decomposed by water, reduces Fehling's solution and potassium permanganate, and, on heating, is converted into yellow bismuth oxide; its sp. gr. is 7.153 to 7.201 at 19°. When heated above the melting point of bismuth in a current of carbon dioxide, it is converted into a grey mixture of bismuth oxide and metallic bismuth.

The oxalate, $\text{Bi}_2\text{O}_3(\text{C}_2\text{O}_4)_2$, when heated in a current of dry carbon dioxide, yields a mixture of the suboxide and metallic bismuth, sp. gr. 8.356 at 19°. This product gives the same chemical reactions as the suboxide, but is shown to be a mixture by measuring the heat evolved on dissolving it in acids (this vol., ii, 451).

E. C. R.

Solubility of Manganous Sulphate. By THEODORE W. RICHARDS and FRANK ROY FRAPPIÉ (*Amer. Chem. J.*, 1901, 26, 75—80. Compare Cottrell, this vol., ii, 12).—The solubility of the pentahydrate of manganous sulphate is 65.19 per cent. at 25°, whilst that of the tetrahydrate is 66.38 at 30.15° and 68.22 per cent. at 35°, the figures in each case representing the number of grams of the anhydrous salt in 100 grams of the solution. These results confirm those of Cottrell, and disprove

those of Linebarger (Abstr., 1893, ii, 417). It was found that manganous sulphate retains traces of water even after being heated for half an hour at 350° , but that at 450° the whole is expelled.

E. G.

Manganic Phosphates. By VICTOR AUGER (*Compt. rend.*, 1901, 133, 94—96).—A *manganic pyrophosphate*, $\text{Mn}_4\text{P}_6\text{O}_{21}\cdot 14\text{H}_2\text{O}$, is obtained by fusing manganese nitrate with phosphoric acid at 210° , extracting the fused mass with water, and adding alcohol to the violet-coloured extract; the salt separates as a buff-coloured, crystalline precipitate which loses $10\text{H}_2\text{O}$ at 185° , and the remaining $4\text{H}_2\text{O}$ at 440° . Cold solutions of alkalis extract phosphoric acid, which appears in solution as a pyrophosphate. Sulphuric acid dissolves it with a violet colour, which becomes red on dilution. Cold phosphoric acid dissolves it; from the violet solution which becomes rapidly colourless, the phosphate $\text{MnPO}_4\cdot \text{H}_2\text{O}$ separates. The preparation of manganic metaphosphate, MnP_3O_9 , is also described (compare Hermann, *Ann. Phys. Chem.*, 1858, 105, 289).

K. J. P. O.

Behaviour of an Iron Cathode in a Solution of Ammonium Nitrate. A New Ferrous Ferric Oxide. By A. KAUFMANN (*Zeit. Elektrochem.*, 1901, 7, 733—741).—When a solution of ammonium nitrate, saturated at 0° , is electrolysed in a cell containing a porous diaphragm, a carbon anode and an iron cathode, with a cathodic current density of 0.00002 ampere per sq. cm., the iron dissolves, forming a golden-yellow solution. When this solution is heated in absence of air, a black, amorphous, magnetic oxide of iron is precipitated. The yellow solution contains ferrous ammonium nitrate, and may be prepared by treating finely divided iron with a concentrated ammoniacal solution of ammonium nitrate. Similar solutions are obtained with other ammonium salts, the more concentrated the solution and the higher the temperature the better are the results obtained. The iron exists in the ferrous ammonium nitrate solution as a complex cation.

The new oxide of iron has the composition $2\text{FeO}\cdot 3\text{Fe}_2\text{O}_3$; it is bluish-black, which distinguishes it from the brownish-black magnetic oxide, Fe_3O_4 . It is best prepared by dissolving crystallised ferrous sulphate (21 grams) in water (220 grams) and 20 per cent. ammonia (22 grams) and boiling, after which potassium nitrate (2.55 grams) is added in portions and the boiling continued for 15 minutes. T. E.

Electrochemical Formation of Alkali Ferrates. By WALDEMAR PICK (*Zeit. Elektrochem.*, 1901, 7, 713—724).—Full details of the experiments described by Haber and Pick (this vol., ii, 103). When iron, especially one of the purer kinds, is used as anode in a solution of an alkali hydroxide, a temporary formation of ferrate occurs; by reversing the current for a short time after the formation of ferrate has ceased, the iron returns to the condition in which it can be oxidised to ferrate, and after several repetitions of the treatment this condition becomes permanent. The same result is obtained by using the iron as anode in a concentrated solution of an alkali hydroxide and passing a very small current for some time. The iron is

found to be covered by a dark grey skin which prevents atmospheric oxidation.

T. E.

Ferrite Solutions. By FRITZ HABER (*Zeit. Elektrochem.*, 1901, 7, 724—726).—Details of the methods used to prove that the liquid obtained by boiling a solution of sodium ferrate contains a compound of ferric oxide, Fe_2O_3 (see this vol., ii, 103).

T. E.

Simultaneous Deposition of Iron and Nickel from Mixed Solutions of their Sulphates. By FRIEDRICH W. KÜSTER (*Zeit. Elektrochem.*, 1901, 7, 688—692).—The smallest *E.M.F.* which will cause deposition of nickel from a solution of nickel sulphate is about 0.1 volt less than that required to deposit iron from a solution of ferrous sulphate, when platinum point cathodes are used. From solutions containing both salts, nickel alone is deposited when the applied *E.M.F.* is just sufficient to produce deposition of nickel from a solution of nickel sulphate, but iron begins to be deposited at a point midway between the deposition points of nickel and iron, and the proportion of iron in the deposit rapidly increases with the *E.M.F.* used. A deposit containing 75 per cent. of iron is obtained from a solution containing equal quantities of iron and nickel, and this composition is almost independent of the *E.M.F.* between fairly wide limits. When working with sensible currents, therefore, iron is deposited more rapidly than nickel, although it requires a larger *E.M.F.* The author suggests that, although the magnitude of the force producing a chemical change may determine it when the velocity is very small, yet at sensible velocities (as Nernst pointed out) a kind of chemical Ohm's law may determine the velocity (velocity = chemical force/chemical resistance) so that the velocity of deposition of iron might exceed that of nickel, although the driving force were less.

T. E.

Cobalt and Nickel Iodates and their Solubility in Water. By A. MEUSSER (*Ber.*, 1901, 34, 2432—2442).—Cobalt iodate crystallises from water in three forms: in the anhydrous state, with $2\text{H}_2\text{O}$ and with $4\text{H}_2\text{O}$ respectively; the trihydrate, pentahydrate, and hexahydrate could not be obtained (compare Clarke, *Abstr.*, 1878, 377, and Ditte, *Abstr.*, 1892, 1388). The tetrahydrate, $\text{Co}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$, forms red crusts of six-sided needles. The dihydrate, $\text{Co}(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}$, was probably obtained by Rammelsberg (*Ann. Phys. Chem.*, 1838, 44, 562) in an impure form. A table and curves of solubilities are given, shewing the variation of solubility of the three forms with changing temperature; at 18° , 0.038 mol. of the tetrahydrate, 0.020 mol. of the dihydrate, and 0.046 mol. of the anhydrous salt are soluble in 100 mols. of water. The solubility of the tetrahydrate increases rapidly with the temperature, the rate of increase becoming greater at higher temperatures; the solubility of the anhydride diminishes with rising temperature, whilst that of the dihydrate increases in nearly direct proportion.

The author differs from Rammelsberg, Clarke, and Ditte with regard to the hydrates of nickel iodate, being able to isolate only the anhydrous form, two dihydrates, and a tetrahydrate. The tetrahydrate, $\text{Ni}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$, forms green, six-sided prisms and loses water, iodine,

and oxygen below 100° . The α -dihydrate forms a crust of greenish crystals, and the β -dihydrate short, lustrous prisms. The anhydrous salt forms microscopic needles, which, in transmitted light, are colourless, but as a powder appears yellow in reflected light.

Curves and tables of solubilities are given for various temperatures, 0.063 mol. of the tetrahydrate, 0.039 mol. of the α -dihydrate, 0.050 mol. of the anhydrous salt dissolve in 100 mols. of water at 30° ; the β -dihydrate is much less soluble than the α -dihydrate. W. A. D.

Electrolysis of Uranium Nitrate. By WILLIAM OECHSNER DE CONINCK and CAMO (*Bull. Acad. Roy. Belg.*, 1901, 321—322. Compare this vol., ii, 104, 105, 164, 165, 390).—The electrolysis of 6—8 per cent. solutions of uranium nitrate yields the black, pulverulent, pyrophoric protoxide; this, when dried in a water-oven, is converted into the orange-coloured hydrate, $U_2O_3 \cdot H_2O$, of the sesquioxide. With a weaker current, the canary-yellow hydrate, $U_2O_3 \cdot 2H_2O$, and the orange-coloured hydrate, $U_2O_3 \cdot H_2O$, are formed. With some solutions, a current of about 1 ampere gives a mixture of the yellow and orange hydrates; with others, the black oxide, U_4O_9 , is obtained, along with one of its hydrates which is violet. The latter in a dry atmosphere slowly changes into the yellow hydrate. The black oxide, U_4O_9 , is very stable, and is thus distinguished from the protoxide; it does not oxidise at 100° , and when strongly heated in hydrogen is reduced to the protoxide.

When solutions of uranium nitrate containing traces of nitric acid are electrolysed, a precipitate is not formed, owing to the oxides initially produced dissolving in the acid present. W. A. D.

Preparation of pure Antimony Hydride. By ALFRED STOCK and WALTHER DOHT (*Ber.*, 1901, 34, 2339—2344).—Pure antimony hydride can be prepared by condensing the dried mixture of antimony hydride and hydrogen (obtained by treating powdered antimony-zinc alloy containing 25 per cent. of antimony with dilute acid) in a U-tube surrounded with liquid air. Pure antimony hydride condenses to a colourless liquid, has a faint smell resembling that of hydrogen sulphide, is decomposed by air, but is not changed by light or moisture. R. H. P.

New Treatment of Niobite: Preparation and Properties of Fused Niobium. By HENRI MOISSAN (*Compt. rend.*, 1901, 133, 20—25).—Niobite was heated with carbon in the electric furnace for 7 or 8 minutes with a current of 1000 amperes and 50 volts, and gave a regulus containing niobium and tantalum, with 2.18 to 2.34 per cent. of combined carbon, but no graphite. The alloy was converted into potassium fluoantilate and potassium fluoxyniobate, which were separated by crystallisation, and the fluoxyniobate was converted into niobium pentoxide. The latter, when heated with carbon in the electric tube furnace with a current of 600 amperes and 50 volts, yields fused niobium, which is somewhat hard, and readily scratches glass and quartz. Its melting point is higher than 1800° . The powdered metal becomes incandescent in fluorine at the ordinary temperature and in chlorine at about 205° , and is attacked by bromine at a somewhat higher temperature, but not by iodine at the softening point of glass. In oxygen at about 400° or air at a higher

temperature, it burns, and yields niobic pentoxide, but sulphur vapour acts superficially only at 600°, and selenium and tellurium have no action at this temperature. Nitrogen, phosphorus, arsenic, and antimony do not act on niobium at 500—600°, but nitrogen forms a yellow nitride at 1200°. When in a state of fusion, the metal combines slowly with carbon, but even when the latter is in excess, a regulus containing graphite is not formed. Hydrogen chloride is decomposed by powdered niobium at a dull red heat, but water vapour and hydrogen sulphide are not decomposed even at 600°, whilst at a red heat ammonia is simply decomposed into nitrogen and hydrogen. Sulphur dioxide is reduced with incandescence at about 600°, and nitrous oxide, nitric oxide, phosphoric oxide, and carbon dioxide are reduced at a dull red heat. Iodine and arsenic pentoxides are reduced at a somewhat lower temperature. When fused with niobium, chromic oxide is reduced and a brittle alloy of niobium and chromium formed. Fused oxidising agents readily attack niobium, but ordinary acids are without action, with the exception of hydrofluoric acid and hot concentrated sulphuric acid, and even these act very slowly. Niobium does not form alloys with sodium, potassium, magnesium, or zinc, but at its melting point it takes up small quantities of iron. C. H. B.

Recovery of Platinum from Platinum Residues. By ADOLF BERTHOLD (*Zeit. angew. Chem.*, 1901, 14, 621—622).—Any deposit is collected on a filter, dissolved in nitro-hydrochloric acid, and the solution evaporated to dryness; the residue is then dissolved in hot water and added to the main filtrate. After adding hydrochloric acid, some zinc dust is introduced, and when the liquid has become colourless, it is carefully poured off from the precipitated platinum black. This is washed first with boiling hydrochloric acid and then repeatedly with boiling water, first by decantation, and then in a weighed Gooch crucible. To completely remove the last traces of potassium, it is ignited, again washed with boiling water until free from chlorine, dried, ignited, and weighed. Finally, it may be converted into platinum chloride solution of known strength. L. DE K.

Mineralogical Chemistry.

Analysis of supposed Italian Bauxites. By CARLO FORMENTI (*Gazzetta*, 1901, 31, i, 452—455).—The author has analysed four samples of supposed bauxite found in Italy, and finds that, although the main constituents are the same as in bauxite, the relative proportions of them are widely different. The samples cannot even be considered as representing poor bauxites, and could not be used for the profitable extraction of aluminium compounds.

T. H. P.

Liveingite, a new Mineral from the Binnenthal. By RICHARD HARRISON SOLLY, with analysis by HENRY JACKSON (*Proc. Camb. Phil. Soc.*, 1901, 11, 239—240).—In general appearance this new mineral resembles the several other sulpharsenites of lead which occur in the white dolomite of the Binnenthal in Switzerland. The crystals are oblique, with pseudo-rhombic habit; in the prism zone they have the angles of sartorite ($\text{PbS}, \text{As}_2\text{S}_3$), and in the dome zone the angles of rathite ($3\text{PbS}, 2\text{As}_2\text{S}_3$). The two individuals of the twinned crystals have respectively a red and a green tarnish on the surface. The following analytical results give the formula $4\text{PbS}, 3\text{As}_2\text{S}_3$:

| Pb. | As. | S. | Fe. | Total. |
|-------|-------|-------|-------|--------|
| 47.58 | 26.93 | 24.91 | trace | 99.42. |

L. J. S.

Manganese Ore Deposits of Queluz, Brazil. By ORVILLE A. DERBY (*Amer. J. Sci.*, 1901, [iv], 12, 18—32).—The manganese ores of the Queluz (Lafayette) district in Minas Geraes occur over a wide area in granitic and gneissic rocks, and are intimately associated with rocks composed wholly or largely of manganese garnet (spessartite). It is shown that the black manganese oxides forming the ore have been derived by the alteration of this garnet. Detailed descriptions are given of the mode of occurrence of the ores, and analyses are given of the garnet rock.

L. J. S.

Synthesis of Boronatrocalcite (Ulexite). By AUGUST B. DE SCHULTEN (*Compt. rend.*, 1901, 132, 1576—1577).—This mineral is prepared artificially by adding a solution of calcium chloride to a large excess of a saturated solution of borax, and allowing the mixture to remain in a closed vessel for 15 to 30 days. At the end of this time, the amorphous precipitate is entirely transformed into acicular crystals, but these are too minute for optical and crystallographical examination. Analysis of this crystallised material gave the same formula as that adopted for the mineral ulexite, namely, $\text{Na}_2\text{O}, \text{CaO}, 5\text{B}_2\text{O}_3, 16\text{H}_2\text{O}$. The crystals are slowly dissolved by cold water. Sp. gr. 1.955. L. J. S.

Brushite from the Island of Mona, West Indies. By CARL KLEIN (*Sitz.-ber. Akad. Wiss. Berlin*, 1901, 720—725).—Wax-yellow crystallised brushite with a perfect cleavage in one direction, occurs in the guano deposits of the island of Mona near Porto Rico. Sp. gr. 2.28. Analysis by Finkener gave

| CaO. | P ₂ O ₅ . | SO ₃ . | H ₂ O. | Total. | H ₂ O at 130°. |
|-------|---------------------------------|-------------------|-------------------|--------|---------------------------|
| 30.83 | 37.96 | 0.49 | 30.88 | 100.16 | 25.17 |

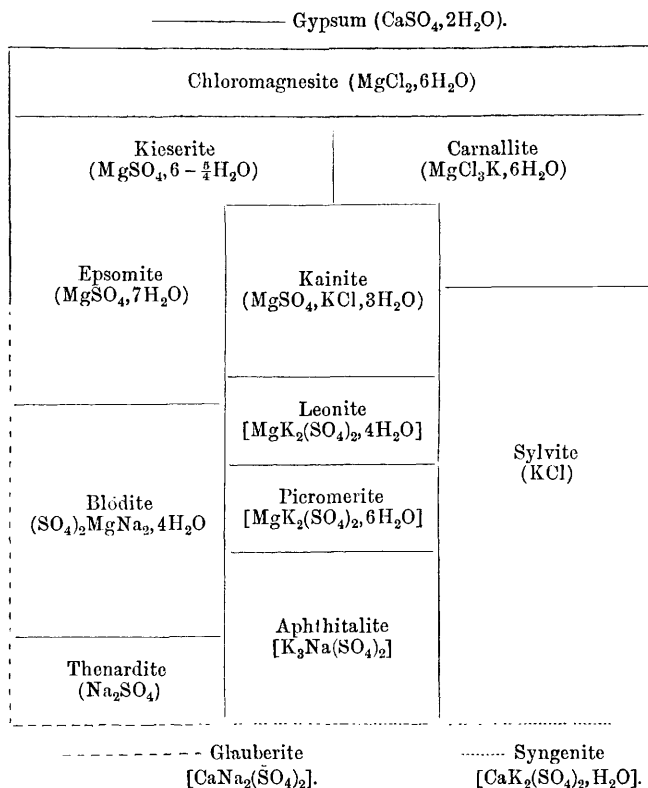
Deducting a little gypsum or anhydrite, this gives the formula $2\text{HCaPO}_4, 5\frac{1}{2}\text{H}_2\text{O}$; the mineral thus appears to differ from brushite ($2\text{HCaPO}_4, 4\text{H}_2\text{O}$) in containing more water, and for this reason the name *stoffertite* is provisionally proposed for it. Crystallographical and optical determinations are given, and those of Lacroix (*Abstr.*, 1897, ii, 505) discussed.

L. J. S.

Crystallisation of Complex Salt Solutions with particular reference to Oceanic Salt Deposits. By JACOBUS H. VAN'T HOFF (*Zeit. angew. Chem.*, 1901, 14, 531—537).—A solution of sodium and

potassium chlorides when evaporated at 25° deposits the excess of one of the salts until the concentration of the solution with respect to NaCl and KCl respectively is 89 and 39 mols. per 1000 mols. of water. The deposit thereafter has the same composition as the solution, and a mixture in these proportions is the ultimate product of the evaporation.

With magnesium and potassium sulphates, the first depositions take place in such a way as to leave a solution containing 38 mols. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 14 mols. of picromerite per 1000 mols. of water and



this mixture then separates out. It is important to notice that in these considerations it is supposed that the deposit is removed from contact with the solution, a condition which is practically attained in the natural deposition, since the formation of crust prevents the action of the solution on the lower layers.

With potassium chloride and magnesium sulphate double decomposition takes place and the following may deposit: potassium sulphate, sylvite, picromerite, magnesium sulphate (hepta- and hexa-hydrates), carnallite, and magnesium chloride. During the deposition, the

composition of the solution alters so as to approach that represented by 2 mols. of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, 12 mols. of $\text{MgCl}_2 \cdot \text{K} \cdot 6\text{H}_2\text{O}$, and 99 mols. of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ per 1000 mols. of water and the solution then dries, leaving a mixture of these in the proportions given.

If to the last mixture sodium chloride be also added, then the following may separate from the solution: magnesium chloride, sylvite, thenardite, magnesium sulphate (with 7, 6, 5, or $4\text{H}_2\text{O}$), picromerite, leonite, blödite, aphthitalite, kainite, and carnallite. The final deposit in this case is also a mixture of carnallite, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$.

When calcium salts are also present then depositions of the following may also take place: gypsum, anhydrite, glauberite, syngenite, and tachhydrite, but this case has not yet been exhaustively investigated.

Assuming that the natural deposition takes place at 25° , the scheme on p. 559 represents (1) 14 minerals which may occur along with sodium chloride, (2) minerals which occur together (contiguous fields).

Thus carnallite may occur with sylvite, but not with aphthitalite; syngenite with sylvite; glauberite with blödite, &c.

J. McC.

[Albite in] Green Schist from Piedmont. By HEINRICH PREISWERK (*Centr. Min.*, 1901, 303—308).—Chlorite- and amphibole-schists, which have been derived from diabases, are of general distribution, and a usual constituent of such rocks is a colourless, perfectly fresh felspar usually recognisable only as a mosaic under the microscope. A green schist at Brusson, Piedmont, contains large crystals of this felspar in association with chlorite, hornblende, epidote, zoisite, &c. Analysis of the felspar (sp. gr. 2.652—2.636) by W. Forsberg gave:

| SiO_2 . | Al_2O_3 . | Fe_2O_3 . | CaO . | MgO . | K_2O . | Na_2O . | Total. |
|------------------|---------------------------|---------------------------|----------------|----------------|------------------------|-------------------------|--------|
| 64.81 | 20.13 | 0.21 | 1.29 | 0.45 | 0.68 | 11.65 | 99.22 |

This indicates a close approach to albite; and specially selected fragments of pure material were found to contain no calcium. Optical determinations also point to the material being nearly pure albite.

L. J. S.

A Mineral from Casal Brunori, near Rome. By FERRUCCIO ZAMBONINI (*Centr. Min.*, 1901, 397—401).—In a few cavities in the lava at this locality was found a greenish-yellow, woolly substance in association with calcite. Under the microscope, it is seen to consist of an aggregate of short rods, of which the optical extinction is straight. The following analysis of this material gives the formula $\text{RO} \cdot \text{R}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 7\text{H}_2\text{O}$; it therefore appears to be identical with the Scotch chlorophæite:

| SiO_2 . | Al_2O_3 . | Fe_2O_3 . | MnO . | MgO . | $\text{K}_2\text{O}, \text{Na}_2\text{O}$. | H_2O . | Total. |
|------------------|---------------------------|---------------------------|----------------|----------------|---|------------------------|--------|
| 37.86 | 13.54 | 13.33 | trace | 6.27 | 2.65 | 26.12 | 99.77 |

L. J. S.

Asbestos from Alilovci, District of Sauskimost. By JOH. GRIMMER (*Geol. Centr.*, 1901, 1, 386; from *Wiss. Mitth. aus Bosnien u. d. Herzegovina*, 1899, 6, 887—889).—The asbestos mined at this locality surrounds and penetrates blocks of limestone of Permian age. There are no amphibole or serpentine rocks in the immediate vicinity, although the latter are found five kilometres west of Alilovci. Analysis by L. Scheiders gave the results under I; Analysis II, by S. Bošnjaković, is of less pure material after being digested with hydrochloric acid and air-dried.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MgO. | CaO. | K ₂ O. | Na ₂ O. | CO ₂ . | H ₂ O. | Total. |
|-----|--------------------|----------------------------------|----------------------------------|------|-------|------|-------------------|--------------------|-------------------|-------------------|--------|
| I. | 54.10 | — | 15.76 | 7.33 | 12.60 | 1.44 | 0.45 | 5.40 | 0.09 | 2.81 | 99.98 |
| II. | 52.35 | 5.47 | 15.36 | — | 10.39 | — | 4.37 | — | — | 10.25 | 98.19 |

L. J. S.

Analysis of Travertine from Vichy. By C. GIRARD and FRED. BORDAS (*Compt. rend.*, 1901, 132, 1423—1426).—Analyses are given of three samples of travertine (calcareous tufa) deposited by the mineral water at Vichy. The material is dirty yellow, and compact or ochreous. It consists mainly of calcium carbonate (91.709—97.169 per cent.), with small amounts of carbonates of magnesium, sodium, potassium, manganese and iron, sodium phosphate, aluminium sulphate, magnesium sulphate, ferric arsenate (trace—0.342 per cent.), silica and insoluble residue, together with traces of copper, barium, lithium and chlorine.

L. J. S.

Physiological Chemistry.

Digestive Power of Gastric Juice. By ALBERT FROUIN (*Compt. rend. Soc. Biol.*, 1901, 53, 590—593).—Variation in the digestive power of gastric juice depends chiefly on the amount of hydrochloric acid. Proteid food increases the secretion of pepsin. W. D. H.

Amylolytic Action of Saliva. By P. BIELFELD (*Zeit. Biol.*, 1901, 41, 360—367).—The amount of ptyalin has no influence on the quantity of sugar formed. The percentage amount of starch in the original solution is also unimportant. The important factor is the absolute quantity of starch; the greater the amount of starch, the greater is the amount of sugar formed. The estimations of sugar were made by Pavy's method. The polarimetric method is inaccurate on account of the high optical activity of the dextrans formed.

W. D. H.

Quantitative Action of Pepsin. By FRIEDRICH KRÜGER (*Zeit. Biol.*, 1901, 41, 378—392).—Maszewski (this vol., i, 178) and Biefeld (see preceding abstract) have independently pointed out that in connection with ptyalin, the amount of ferment present is of little or no importance. Quantitative estimations of ptyalin and other ferments hitherto published are therefore to be regarded with suspicion. It

is important, however, to ascertain whether the same law holds for other ferments, and the present research relates to pepsin. There are differences between pepsin and ptyalin. In the case of pepsin, the amount of proteolytic products increases with the amount of pepsin, but not proportionately. The activity of pepsin increases with decrease in the concentration of the original proteid solution, but not proportionately; the most important factor, however, as in the case of ptyalin, is the total amount of proteid present. W. D. H.

Lipase. By MAURICE HANRIOT (*Compt. rend. Soc. Biol.*, 1901, 53, 369).—By fractional precipitation of serum with ammonium sulphate, iron and lipase are found in the first portion of the precipitate. If zinc powder is added to serum, ferric salts are reduced to ferrous, and the power of the lipase is lessened; this, however, returns by agitation with air. The action of lipase is inhibited by acids and restored by alkalis; this is explained by supposing that the acid displaces the iron with which the lipase is in combination. W. D. H.

Intracellular Digestion and Enzymes in Actiniæ. By FÉLIX MESNIL (*Ann. Inst. Pasteur*, 1901, 15, 352—397).—The fluid in the cœlenteric cavity of *Actiniae* has no digestive action. Digestion is accomplished in the same cells as those which form the ferments. By destroying the cells, the enzymes may be extracted. These are of various kinds, proteolytic, rennin-like, diastatic, and hæmolytic, and although intracellular, they obey the same laws as extracellular ferments. W. D. H.

Cause of the Increase of Proteid Decomposition during Inanition. By FRIEDRICH N. SCHULZ (*Zeit. Biol.*, 1901, 41, 368—377).—Polemical; mainly directed against Kaufmann (this vol., ii, 254). W. D. H.

Absorption of Fat. By EDOUARD PFLÜGER (*Pflüger's Archiv*, 1901, 86, 1—46).—One hundred c.c. of fresh ox-bile dissolve 4 or 5 grams of oleic acid; the amount rises to more than 10 grams when an equivalent amount of sodium hydroxide is also added. On being warmed to 37° for a day, 17 to 19 per cent. of the fatty acid is saponified. Bile does not accelerate the saponification of oleic acid by soda. If stearic acid is warmed to 37° for 4 to 5 days with sodium hydroxide, there is no trace of saponification, but if oleic acid is also added, saponification goes on rapidly, and this is much more marked on the addition of bile. If 100 c.c. of bile are mixed with 10 grams of stearic and 10 grams of oleic acid and an equivalent amount of dilute sodium hydroxide solution, about 15 grams of fatty acid are brought into a condition which is soluble in water. Neutral soaps dissolved in water are precipitated by the addition of much water, and free fatty acid is liberated; thus soaps undergo hydrolytic dissociation. During fat absorption, the reaction of the contents of the small intestine is sometimes acid, sometimes alkaline. W. D. H.

Action of Alcohols on the Arterial Blood Stream. By HANS BUCHNER, F. FUCHS, and L. MEGELE (*Arch. Hygiene*, 1901, 40, 347—374).—Methyl alcohol is a stronger, and *n*-propyl alcohol a much stronger

antiseptic than ethyl alcohol. The beneficial effect of alcohol bandages cannot, however, be explained by germicide action, for only traces of the alcohol penetrate the skin. The alcohol stimulates the skin, dilates the vessels locally, increases the flow of blood through the deeper tissues, and so confers on them greater resistance to infective agents. W. D. H.

Formation of Lactic Acid in the Blood. By LEON ASHER and HOLMES C. JACKSON (*Zeit. Biol.*, 1901, 41, 393—436).—Katabolic processes are not qualitatively different in artificial transfusion, and under normal conditions. The formation of lactic acid is related to proteid decomposition in the cells, and it does not apparently originate from dextrose. Incomplete oxidation of carbohydrate owing to lack of oxygen is not the cause of the formation of lactic acid. W. D. H.

A new Reducing Substance in the Blood. By PAUL MAYER (*Zeit. physiol. Chem.*, 1901, 32, 518—530).—Ox-blood contains a glycuronic acid compound as a normal constituent. This substance is a reducing agent and yields an osazone which melts at 159—164°. The existence of this substance will probably explain some of the results obtained by Pavy and Siau (this vol., ii, 257); possibly the osazone they found which melts at 157°, and which they consider is derived from isomaltose, in both blood and diabetic urine is really derived from glycuronic acid. Glycuronic acid increases in the urine in diabetes. W. D. H.

Sugar Formation after administration of Proteids. By ERNST BENDIX (*Zeit. physiol. Chem.*, 1901, 32, 479—503).—By feeding dogs, freed from glycogen, on proteids, and subsequently administering phloridzin and estimating the sugar/nitrogen quotient, it was found that as much or more sugar was produced when the proteid given was casein or gelatin as when egg-albumin was given. In other experiments, the glycogen in the animal's body was estimated, and here again glycogen was formed abundantly on a proteid diet, even when the proteid was one like casein or gelatin, which contains no carbohydrate radicle. W. D. H.

A Glycolytic Enzyme in Muscle. By SIR T. LAUDER BRUNTON and HERBERT RHODES (*Proc. Roy. Soc.*, 1901, 68, 323—326).—Glycerol extracts of muscle are slightly glycolytic in relation to dextrose. Muscle juice squeezed out at high pressure is more so. This power is destroyed by boiling, and is not due to bacteria. Attempts were made to isolate the enzyme by precipitation with alcohol, but without success. W. D. H.

Chemical Nature of the Tissues. By ALEXANDRE ÉTARD (*Ann. Inst. Pasteur*, 1901, 15, 398—408).—Protoplasm of any origin contains a proteid substance termed *protoplasme*, in which about 16 per cent. of nitrogen is present.

When treated with sulphuric acid, the bone tissue, freed from calcium salts, yields various hydrolytic products, amongst which are glycine and leucine. R. H. P.

Immunity in relation to the Pancreas and its Ferments. By GEORGE DEAN (*Trans. Path. Soc.*, 1901, 52, 127—134).—Experi-

ments were made by subcutaneously injecting tryptic solutions in goats. The results show that an increase over the normal antitryptic action of the serum can be obtained by a process of immunisation. The increase is not a great one, and there is no enormous accumulation of the anti-compound in the blood, as in the case of bacterial antitoxins. Ehrlich's explanation of the failure to obtain anti-rennin of great strength seems to be applicable to antitrypsin. W. D. H.

Active Principle of the Suprarenal Gland. By T. B. ALDRICH (*Amer. J. Physiol.*, 1901, 5, 457—461).—Takamine (*Therap. Gaz.*, 1901, 221) has separated the active principle from suprarenal glands, and named it *adrenalin*. 0.000001 gram per kilo. of body weight raises the blood pressure. The present author has independently prepared the same substance by another method, and obtained it in a crystalline form. Its formula is $C_9H_{13}O_3N$. Abel's epinephrin is possibly a benzoyl derivative of it. W. D. H.

Elimination of Sodium Salicylate by the Bile. By GEORGES LIROSSIER (*Compt. rend. Soc. Biol.*, 1901, 53, 365—367).—In three experiments on dogs dosed with sodium salicylate, the drug was estimated in blood, liver, bile, and urine. The amount in the urine exceeded that in the bile in two experiments, in the third there was more in the bile. The amount in the bile is insufficient to exert any antiseptic action. W. D. H.

Non-permeability of the Wall of the Urinary Bladder. By OTTO COHNHEIM (*Zeit. Biol.*, 1901, 41, 331—340).—In the intestinal wall, the stream of liquid is in one direction only; in the peritoneum, diffusion resembles that which occurs through parchment paper. In the urinary bladder, the liquid contained within it alters no more than it would in a glass vessel. The bladder wall is not a diffusion membrane, or a semipermeable membrane, and is not permeable to water. These differences furnish evidence of the 'physiological component' in the movement of liquid through living animal membranes. As soon as these three membranes are poisoned with sodium fluoride, the differences between them disappear, and they all behave like diffusion membranes. W. D. H.

Rôle of Leucocytes in Excretion. By HENRY STASSANO (*Compt. rend.*, 1901, 133, 110—113).—Leucocytes, like endothelial cells, are capable of ingesting and incorporating with themselves many poisonous materials, both inorganic and organic. They also assist elimination by discharging such compounds combined with nucleo-proteid into the blood plasma, excretion being finally performed either in the intestinal or renal tract. Narcotics lessen diapedesis, but not the capacity of absorption of the leucocytes. W. D. H.

Action of Currents of high frequency on the Secretion of Urine. By DENOYÉS, MARTRE, and ROUVIÈRE (*Compt. rend.*, 1901, 133, 64—67).—Currents of high frequency applied for a short time (10—25 minutes) daily increase the quantity of urine, urea, uric acid, and inorganic salts secreted daily. This increase lasts to a less degree for the three days following the treatment. Experiments with analytical tables are given for three individuals. W. D. H.

'Organic Chlorine' in the Urine. By JULES VILLE and JOSEPH MOITTESSIER (*Compt. rend. Soc. Biol.*, 1901, 53, 673—675).—Although the precipitation of small quantities of chlorides by silver nitrate may be prevented by the presence of urea and other extractives of the urine, there is no evidence of the existence of organic chlorine compounds in the urine.

W. D. H.

Variations in the Excretion of Nitrogen and Chlorides during Insufficient Nutrition. By ADOLPHE JAVAL (*Compt. rend. Soc. Biol.*, 1901, 53, 551—553).—In a healthy young man who submitted to a sparse diet for some days, the body lost sodium chloride during the first three days, after which there was retention. The addition of more salt to the diet led to a retention of more proteid. Alcohol and iodides had no action either on the salt or nitrogen of the urine.

W. D. H.

Influence of Caffeine on Nitrogenous Excretion. By H. RIBAUT (*Compt. rend. Soc. Biol.*, 1901, 53, 393—395).—In small doses, caffeine diminishes, in large doses increases, nitrogenous excretion in dogs. This may explain previous contradictory statements on the subject.

W. D. H.

Influence of Nitrogenous Food on the Excretion of Uric Acid. By E. MAUREL (*Compt. rend. Soc. Biol.*, 1901, 53, 427—430).—If the food contains but little nitrogen, uric acid diminishes in the urine. It is regarded as a product of incomplete katabolism.

W. D. H.

Excretion of Kynurenic Acid. By LAFAYETTE B. MENDEL and EDWARD C. SCHNEIDER (*Amer. J. Physiol.*, 1901, 5, 427—456. Compare this vol., ii, 259).—Kynurenic acid is always found in the urine of fasting dogs, and when putrefaction in the intestine is checked by calomel. Iodoform stimulates proteid metabolism, and increases the output of kynurenic acid. Salol and naphthalene, and in one case sterilised meat, check the output without any marked decrease of nitrogenous excretion. Phosphorus, phloridzin, and less constantly sodium oxalate and hydrazine sulphate, stimulate proteid katabolism and increase the kynurenic acid excreted. The ingestion of gelatin, elastin, cartilage, ovomucoid, and thymus does not lead to formation of kynurenic acid; that of pancreas, lymph glands, fibrin amandin (a pure vegetable proteid) does so. Proteose feeding leads to a large increase of the acid, but products of proteolysis which do not give the biuret reaction do not. Glycocine does not interfere with its elaboration. Attempts to obtain evidence of the synthesis of the acid from tyrosine failed.

W. D. H.

Influence of Diet on the Phosphoric Acid and Sodium Chloride of the Urine. By E. MAUREL (*Compt. rend. Soc. Biol.*, 1901, 53, 430—431).—The quantity of phosphates in the urine is approximately the same as in the food. The same is true for sodium chloride; most of the salt ingested leaves the body in 24 hours; the excretion is complete in 2 days.

W. D. H.

Composition of Œdema-fluid. By J. BAYLAC (*Compt. rend. Soc. Biol.*, 1901, **53**, 519—521).—A number of analyses of dropsical fluid is given. No diagnostic difference between the fluid in cases of kidney and heart disease was noted. W. D. H.

Albumins in Dropsical Pus. By F. MALMÉJAC (*J. Pharm.*, 1901, [vi], **14**, 15—17).—Analyses are given of pus taken from a dropsical patient at different periods; the albumins differ considerably, the serum-albumin in the sample taken first being almost replaced by Patein's albumin in the sample taken a month later. R. H. P.

Analysis of Pus from a Tumour in the Kidney. By GUSTAVE PATEIN and POYOU (*J. Pharm.*, 1901, [vi], **14**, 54—56).—Analyses are given of the pus from a tumour in the kidney and of urine passed by the patient. Although both contained dextrose, the composition of the pus was quite different from that of the urine. R. H. P.

Analysis of Calculi from the Pancreas. By LEGRAND (*J. Pharm.*, 1901, [vi], **14**, 21—22).—An analysis of some calculi from the pancreas of a diabetic patient gave 1·7 per cent. of sodium chloride, 2·4 per cent. of disodium phosphate, 93·1 per cent. of calcium carbonate, and 0·7 per cent. of organic matter; tyrosine was not found. R. H. P.

Relation between Chemical Constitution and Physiological Action in the Piperidine Series. By RICHARD WOLFFENSTEIN and EDUARD WOLFFENSTEIN (*Ber.*, 1901, **34**, 2408—2410).—The physiological action of the following three groups of piperidine derivatives has been investigated.

(1) Alkyl derivatives with alkyl linked to carbon; (2) Alkyl derivatives with alkyl linked to nitrogen; (3) Acyl derivatives. The experiments were carried out on rabbits and frogs. The two classes of alkyl derivatives are qualitatively similar in their action, but quantitatively different, whilst the acyl derivatives have a different type of action. The paper contains a list of the lethal doses of the various compounds investigated. K. J. P. O.

Action of Peroxides on Toxins. By NATALIE SIEBER (*Zeit. physiol. Chem.*, 1901, **32**, 573—591).—The peroxides of calcium and hydrogen remove the poisonous characters of tetanus-toxin, diphtheria-toxin, and abrin. Animal and vegetable oxydases have the same action on the two first-named toxins, but not on abrin. This action of oxydases occurs, not only *in vitro*, but also by simultaneous injection *in vivo*. Potassium nitrate extracts no oxydase from the fibrin of normal horse's blood, but it does from the fibrin of the blood of horses rendered immune to diphtheria. Extracts which are not active to guaiacum tincture are also inactive towards toxins. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Chemical Stimulants. The Function of Zinc and Copper in the Nutrition of *Aspergillus Niger*. By ANDREAS RICHTER (*Centr. Bakt. Par.*, [ii], 1901, 7, 417—429).—Zinc sulphate added to nutrient solutions in which *Aspergillus niger* is grown diminishes the dry yield until the dilution reaches about 350 litres per gram-molecule of zinc salt and then acts as a stimulant, the growth produced being about double that formed in the absence of zinc. Copper sulphate, on the other hand, also acts as a poison until about the same degree of dilution is attained, but then does not act as a stimulant but as a slightly depressing agent, even in dilutions of 150,000,000 litres per gram-molecule. The directly poisonous effect of both salts is probably to be attributed to the action of undissociated molecules, whilst the stimulating effect of the zinc salt, and the slightly depressing effect of the copper salt are due to the ions present in the dilute solutions.

A. H.

Fermentation of Glucose by *Bacterium Icteroides*. By ARTHUR HARDEN (*Trans. Path. Soc.*, 1901, 52, 115—117).—The characteristics of the action of the *Bacterium icteroides* on dextrose is indistinguishable from that of the *Bacillus coli communis* (*Trans.*, 1901, 79, 612).

W. D. H.

Indole-like Reaction given by Cultures of the Diphtheria and Pseudo diphtheria Bacilli. By RICHARD T. HEWLETT (*Trans. Path. Soc.*, 1901, 52, 113—114).—The pink reaction obtained by the addition of a strong acid and a weak nitrite solution to cultures of the diphtheria and pseudo-diphtheria bacilli is not due to indole, for the substance which gives the reaction is not volatile. Further investigation showed that the substance which gives the reaction is scatole-carboxylic acid.

W. D. H.

Influence of Chemical Reaction on the Bactericidal Action of Serum. By A. HEGELER (*Arch. Hygiene*, 1901, 40, 375—381).—The bactericidal power of active rabbit's serum is unaltered by small additions of sodium carbonate, but if the serum is inactive, the addition inhibits the increase of typhoid bacilli. Small additions of acid have no influence, but if sufficient acid is added to render the serum distinctly acid, the power of the serum to kill these bacilli is completely lost.

W. D. H.

Preparation of Bottom Fermentation Yeasts having the Property of Fermenting at High Temperatures and the Method of employing them. By GEORGES JACQUEMIN (*Bull. Soc. Chim.*, 1901, [iii], 25, 734—736).—The ordinary bottom fermentation yeasts were cultivated through a large number of generations in worts in which the acidity was gradually increased and the temperature progressively raised; the acid added was either tartaric, citric, or

lactic, and the final concentration of acid equivalent to 7 grams of tartaric acid per litre, the final temperature being 20—25°. The yeast finally obtained was able to cause vigorous fermentation at 20—25°, and retained this property after being grown for several generations in a neutral wort. Details are given for using this yeast for the preparation of a bottom fermentation beer, which need not, like the beers ordinarily obtained with bottom yeasts, be kept at a low temperature, either for storage or transit.

W. A. D.

Influence of Oxygen on the Fermentation produced by different Species of Yeast. By D. IWANOWSKI and S. OBRASTZOFF (*Centr. Bakt. Par.*, [ii], 1901, 7, 305—312).—Three species of yeast, *S. Pombe*, *S. ellipsoideus*, I., and *S. cerevisiae*, I., were cultivated in solutions containing peptone, inorganic salts, and about 5 per cent. of sucrose, parallel experiments being made (1) in a current of air and a current of nitrogen; (2) in an atmosphere of air and an atmosphere of nitrogen, the liquid being left at rest and not disturbed by a current of the gas. After about 48 hours, unfermented sugar being still present, the dry weight of the yeast and the residual sugar were estimated, the solutions having been inoculated with equal weights of the same culture of yeast. From the numbers thus obtained was calculated the fermentation energy (the weight of sugar decomposed by 1 gram of yeast). In no case was the presence or absence of oxygen found to produce any appreciable difference in the fermentative energy of the yeasts employed.

In the experiments of the second series, only a trace of yeast was sown into the solution, and in these cases it was also found that the ratio of yeast produced to sugar decomposed (Pasteur's ratio) was not affected by the presence or absence of oxygen. The experiments of Korff (*Centr. Bakt. Par.*, [ii], 1898, 4, 465), who found that the effect of oxygen varied on different races of the same species of yeast, are probably inaccurate.

A. H.

Invertase and Maltase in Yeast. By THOMAS BOKORNY (*Chem. Zeit.*, 1901, 25, 502—504. Compare this vol, i, 437).—Yeast maltase has its maximum action at 40°, and is destroyed after 30 minutes at 55°; 0.01 per cent. silver nitrate, 0.02 mercuric chloride, 0.5 sulphuric acid, 1.0 hydrochloric acid, 1.0 oxalic acid, 1.0 sodium hydroxide, 1.0 formaldehyde, and 1.0 per cent. phenol all destroy the enzyme after 24 hours' contact. Turpentine water, 1 per cent. thymol, and 5—10 per cent. alcohol destroy the activity of the enzyme to a large extent.

Invertase is destroyed when heated to 70°, and slowly when heated to 50°; also by 0.1 per cent. silver nitrate, 0.5 mercuric chloride, 5.0 oxalic acid, 1.0 per cent. sodium hydroxide, but not by 0.1 per cent. mercuric chloride, 0.5 sulphuric acid, 0.5 lactic acid, 1.0 oxalic acid, 1.0 hydrochloric acid, 1.0 acetic acid, 0.5 sodium hydroxide, 5.0 formaldehyde, 1.0 phenol, 0.1 per cent. thymol, turpentine water, chloroform water, or absolute alcohol.

J. J. S.

Selection of Carbohydrates by different Yeasts during Alcoholic Fermentation. By WILHELM KNECHT (*Centr. Bakt. Par.*, [ii], 1901, 7, 161—167, 215—228).—Yeast of two varieties (*Frohberg* type

and *Saaz* type of Nürnberg yeast) was cultivated in yeast water and in asparagine solution supplied with the necessary salts in presence of varying amounts of dextrose and lævulose, in order to ascertain what effect varying proportions of these two sugars exerted on the growth and fermentative power of the yeast, and whether the yeast exerted a selective action on the sugars.

The effect produced by variation in the total and relative amounts of the two sugars was found to vary with the kind of yeast and with the nature of the nitrogenous nourishment. Yeast water proved to be decidedly more favourable for the reproduction of the yeast than asparagine. When pure sucrose, which is converted into equal parts of dextrose and lævulose, is used, the dextrose is fermented more rapidly than the lævulose, as has been found previously by Prior. In presence of 8.19 per cent. of dextrose and 1.03 of lævulose, the amount of dextrose fermented in 8 days was 10 times that of the lævulose, and this relation only varied slightly in the different media and for the two varieties of yeast. On the other hand, and in presence of 8.22 per cent. of lævulose and 0.82 per cent. of dextrose, the amount of lævulose fermented in 4 days was, in some cases, as much as 24 times as great as that of the dextrose. When the results are expressed in terms of the amounts fermented by 1,000,000 cells, it may be said that in the most favourable case, in presence of excess of dextrose, 9 parts of dextrose are fermented for 1 of lævulose, whilst in presence of excess of lævulose, 13 parts of lævulose are fermented for 1 of dextrose. The author, however, concludes that the differences in the rapidity of the fermentation of the different sugars are entirely due to physical laws, as already stated by Prior.

A. H.

Nitrification and Denitrification. By ALFRED BEDDIES (*Chem. Zeit.*, 1901, 25, 523—524. Compare Abstr., 1900, ii, 34).—Sterilised sand, containing calcium carbonate (0.2 per cent.) and ammonium sulphate (N=0.1 per cent.), was inoculated with nitrifying and with denitrifying organisms, and the loss of nitrogen determined. Addition of unsterilised sand caused a loss of half the nitrogen in 10 days, whilst straw extract caused a loss of 60 per cent. in about the same time. Inoculation with a pure cultivation of nitrifying organisms resulted in the almost complete conversion of the nitrogen into nitric nitrogen in 8 days. With straw extract, in conjunction with nitrifying organisms, there was a loss of 40 per cent. of the nitrogen, 20 and 40 per cent. being recovered in the form of nitrous and nitric acids respectively. Addition of a strong humus solution (from peat) along with straw extract reduced the loss due to straw extract to 30 per cent.; 30 and 40 per cent. of nitrogen remained as nitrous and nitric acids. When the sand, to which humus and straw extract were added, was also inoculated with nitrifying organisms, no loss of nitrogen took place, 90 per cent. being recovered in the form of nitric, and 10 per cent. as nitrous, acid.

N. H. J. M.

Humidity of Soils and Denitrification. By ERCOLE GIUSTINIANI (*Ann. Agron.*, 1901, 27, 262—285).—Denitrification is most energetic in liquids at a temperature which is injurious to the activity of nitrifying organisms.

As regards the effect of moisture, it was found that in sand the energy of nitrification of ammonium sulphate was directly proportional to the amount of moisture, when this varied from 0—16 per cent.; denitrification of sodium nitrate only took place when the percentage of moisture was less than 10, and was greatest in presence of 2 per cent. of moisture. As compared with nitrification, denitrification was very limited in these experiments. Similar results were obtained in soil.

In the case of soil containing little moisture, denitrification is proportional to the amount of organic matter. N. H. J. M.

Germination of Wheat Grain treated with Copper Sulphate. By E. DEMOUSSY (*Ann. Agron.*, 1901, 27, 257—261. Compare this vol., ii, 266 and 335; and Devaux, *Compt. rend.*, 1901, 132, 719).—Notwithstanding the great sensitiveness of plants to copper salts, the treatment of seeds with copper sulphate is, in practice, without injurious effects, owing to the diffusion into the soil of the traces of copper salt adhering to them. N. H. J. M.

Respiration of Quiescent Seeds. By R. KOLKWITZ (*Chem. Centr.*, 1901, ii, 136; from *Ber. bot. Ges.*, 19, 285—287).—Experiments on the respiration of barley grains have been made by means of an apparatus allowing of the exact estimation of small quantities of carbon dioxide. From grains containing 11—15 per cent. of water, only 0.33 to 1.5 mg. of carbon dioxide were obtained per day and per kilogram, but by increasing the quantity of water, respiration was increased, thus grains containing 33 per cent. expired about 2 grams for the same time and weight. Rise of temperature and addition of oxygen also accelerate respiration. The respiration of the embryo is about three times that of the endosperm. Coarse maceration of the dry grains causes increase of respiration, but further division has the reverse effect. Respiration is stopped by heating the coarse meal at 100°, or by treating with 96 per cent. or with absolute alcohol. By moistening the grains with water in which toluene has been shaken, energetic respiration is induced, but thymol water, on the other hand, has no effect. Mercuric chloride destroys vitality, but does not entirely prevent a very slight evolution of carbon dioxide (compare Hahn, this vol., ii, 121). E. W. W.

Influence of Sodium Fluoride on the Action of Seminase on the Carbohydrates in the Horny Albumens of the Seeds of Leguminosæ. By HENRI HERISSEY (*Compt. rend.*, 1901, 133, 49—52).—Seminase (*Abstr.*, 1900, i, 320, ii, 35, 233) exists in the seeds of *Trigonella Foenum-graecum*, *Robinia Pseud-acacia*, *Ulex europæus*, *Cytisus Laburnum*, *Sarothamnus scoparius*, as well as in lucerne and indigo. Under ordinary conditions, the action of this ferment on the carbohydrates of the horny albumen of the seeds is slow, but in presence of sodium fluoride (1.5 in 100) it is much more rapid, and can be utilised for the preparation of mannose, which is readily isolated by means of phenylhydrazine. Potassium and ammonium fluorides, and potassium and sodium hydrogen fluorides, do not give such good results. C. H. B.

Carbohydrate Metabolism in Winter Leaves. By FRIEDRICH CZAPEK (*Chem. Centr.*, 1901, i, 1295; from *Bot. Zeit.*, 19, 120—128).—The minimum concentration of sugar solutions with which floating evergreen leaves, free from starch, can produce appreciable amounts of starch grains in the chloroplast, is raised by low temperatures. In experiments with various winter leaves, it was found that, whilst at 0° to 2° abundance of starch was produced with 10 per cent. sucrose, at 16° to 18° there was a production of starch with 2 per cent. solutions.

N. H. J. M.

Vegetation of *Nostoc Punctiforme* in presence of different Carbohydrates. By RAOUL BOUILHAC (*Compt. rend.*, 1901, 133, 55—57. Compare Abstr., 1899, ii, 46 and 238; and Radais, *ibid.*, 1900, ii, 362).—In experiments with different carbohydrates, it was found that saccharose, maltose, and starch may be substituted for dextrose for cultivating *Nostoc*; very little growth was obtained in presence of lactose, and lævulose is unsuitable. The available carbohydrates are those which readily yield dextrose when hydrolysed; this is probably effected by diastases, secreted either by nitrogen-fixing bacteria present on the surface of the plant or by the *Nostoc* itself.

Negative results were obtained with arabinose, xylose, galactose, sorbose, trehalose, melezitose, raffinose, mannitol, glycerol, dulcitol, perseitol, gum arabic, and dextrin.

N. H. J. M.

Fixation of Metals by Cell Walls. By H. DEVAUX (*Compt. rend.*, 1901, 133, 58—60).—Plant stems from which the potassium and calcium were completely extracted by acidified water were found to absorb appreciable amounts of potassium, lithium, sodium, calcium, strontium, barium, iron, nickel, cobalt, cadmium, copper, lead, and silver from their salts, which were not removed by washing with distilled water. The solubility of the salt and the nature of the acid seem to be without influence when stems saturated with potassium or lithium are placed in solutions of other salts (copper, iron, or cobalt sulphates, &c.). The original metal is displaced by the second. The process may be reversed; alkali metals in neutral solutions take the place of calcium, although the calcium resists the action of pure water. Heavy metals and metals of the alkaline earths seem, however, to be held with greater tenacity than alkali metals.

Iron is completely fixed, and is not affected by eight hours' contact with concentrated solutions of alkali salts or salts of the alkaline earths.

N. H. J. M.

New Chromogen producing a Carmine-red Dye. By HANS MOLISCH (*Chem. Centr.*, 1901, i, 1295; from *Bot. Zeit.*, 19, 149—152).—*Schenckia blumenaviana*, a rubiaceous plant of Brazil, produces a red dye in all parts when it dies naturally, or when killed by chloroform or alcohol vapour, or by 20 per cent. alcohol. The alcoholic solution shows a blue fluorescence, which is also produced by treating the leaves with 1 per cent. sulphuric acid or acetic acid, and by extracting them with hot water. The fluorescence disappears when

potassium hydroxide or ammonia is added. The leaves of the plant remain green in ammonia vapour.

The chromogen may be extracted from the fresh leaves by water free from air at 27°; the fluorescent solution gradually becomes carmine-red when exposed to air. Dead leaves yield a fluorescent solution, but no dye.

The chromogen is not rubian, and the dye is not alizarin or purpurin. N. H. J. M.

New Alkaloid from the Elder Tree. By F. MALMÉJAC (*J. Pharm.*, 1901, [vi], 14, 17—19).—The bark of the elder (*Sambucus nigra*) possesses a well-known diuretic and purgative action; this is probably due to the alkaloid *sambucine*, which has been extracted from the bark, and also from the fresh leaves, by Stas' method. An aqueous solution of the *hydrochloride* gives a yellow-white coloration with Tanret's reagent and a brown one with Bouchardat's. *Sambucine* is very deliquescent, gives the usual precipitates with alkaloidal reagents, and tastes bitter. In addition to the alkaloid, the author also obtained from the bark a *tannin*, a purgative *resin*, which smelt like scammony, and a yellowish-red *oil*, which had a strong elder-like odour.

R. H. P.

Milk from [Cows grazing on] the Plateau of Sétif (Algeria). By F. MALMÉJAC (*J. Pharm.*, 1901, [vi], 14, 70—74).—The milk from cows grazing off poor and dried-up grass on the Plateau of Sétif, in Algeria, is compared with that from cows fed on rich forage. The total solids vary in the former from 14.25 to 11.62 per cent., in the latter from 14.90 to 13.76; the fats from 3.50 to 3.33 and from 4.90 to 4.05; the sugar (principally lactose) from 4.46 to 3.13 and from 4.54 to 3.33; the ash from 0.90 to 0.60 and from 0.93 to 0.82; the proteid matter from 5.64 to 4.53 and from 5.55 to 4.47.

R. H. P.

Composition and Nutritive Value of the principal Vegetables. By BALLAND (*Rev. Intern. Falsific.*, 1901, 14, 76—78).—More than seventy analyses of various vegetables and parts of vegetables are given. Determinations were made of the dry matter, nitrogen, fat, extract, and cellulose, and, in most cases, of the sugar and acidity also.

The most nutritious vegetables are potatoes and artichokes; then, mushrooms, salsify, asparagus, cauliflower, cabbages, peas and haricots, spinach, sorrel, and lettuce. Other vegetables have very little nutritive value. N. H. J. M.

Food Requirements of Cultivated Plants. By EMIL GODLEWSKI (*Chem. Centr.*, 1901, i, 1247—1248; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 4, 479—536).—Plot experiments with exhausted soil, in which wheat, rye, potatoes, and barley were partially manured. Although the soil contained about the same amounts of K_2O and P_2O_5 soluble in 25 per cent. hydrochloric acid, phosphatic manure had hardly any effect, whilst potassium manures were very effective. In absence of potassium manures, potatoes had a tendency to premature loss of leaf, and this was increased by applying nitrogen and

phosphoric acid. Nitrogenous and phosphatic manures may diminish the yield and injure the quality of potatoes when potash is deficient.

When potassium is deficient in soils, the relations of $K_2O:N$ and $K_2O:P_2O_5$ in potato tubers are reduced, and when nitrogen is deficient, the relation of nitrogen to nearly all the ash constituents is reduced. The relation of $K_2O:N$ depends partly on the variety and on climatic conditions.

The analysis of barley straw gives better indications than the grain as to the composition of the soil. When the dry matter contains less than 1 per cent. of potash, it is to be attributed to deficiency of potash in the soil. The normal relations of the different constituents are $K_2O:N:P_2O_5:CaO:MgO=100:50:30:40:10$. Deficiency of nitrogen only affects the relation of nitrogen to phosphoric acid.

N. H. J. M.

Variations in the Amounts of Nutritive Substances in Oats. By ALBERT ATTERBERG (*J. Landw.*, 1901, 49, 97—172. Compare Abstr., 1888, 317).—Results of analyses of oats may give some indications as to the relative amounts of nutritive substances in the soil, but any conclusions drawn from the results must always be more or less uncertain. It is, however, always possible to ascertain which constituent is taken up each year in the relatively smallest amount, and which in greatest amount.

The oats should be analysed before they are ripe, as in ripening a loss of potassium salts often takes place.

The following numbers show the amounts of the different constituents found in ripe oats:

| | In grain. | | In straw. | | |
|----------------|-----------|------------|-----------|-----------|-----------|
| | N. | P_2O_5 . | K_2O . | CaO. | MgO . |
| Lowest . . . | 1.20—1.36 | 0.37—0.50 | 0.28—0.73 | 0.14—0.21 | 0.08—0.13 |
| Low | 1.37—1.54 | 0.51—0.63 | 0.74—1.20 | 0.22—0.31 | 0.14—0.18 |
| Mean | 1.55—1.73 | 0.64—0.76 | 1.21—1.69 | 0.32—0.43 | 0.19—0.25 |
| High | 1.74—1.94 | 0.77—0.90 | 1.70—2.20 | 0.44—0.57 | 0.26—0.33 |
| Highest . . . | 1.95—2.32 | 0.91—1.09 | 2.21—2.81 | 0.58—0.75 | 0.34—0.42 |

N. H. J. M.

Experiments with German, English, and French Mangels. By FERDINAND WOHLTMANN (*Bied. Centr.*, 1901, 30, 468—470; from *Zeit. landw. Ver. Rheinpreussen*, 1900, 17, No. 14. Compare Abstr., 1900, ii, 501).—The results of experiments with German (11), French (5), and English (4 varieties) mangels are given. The highest percentage of sugar (6.95), as well as the greatest yield of sugar per acre, was obtained with an English variety (mammoth long red).

The manurial effect of "martellin," which consists chiefly of potassium silicate, was compared with that of potassium chloride. Potassium chloride proved to be the better manure, but it is possible that the silicate may have a considerable after effect.

N. H. J. M.

Effect of various Carbonaceous Compounds on the amount of Nitrogen in Soil, and on the development of Plants. By MAX GERLACH (*Bied. Centr.*, 1901, 30, 446—449; from *Jahresber. landw. Versuchs-Stat. Posen*, 1899—1900, 10).—Unmanured soil recently taken from a field gave greater yields of white mustard and rye than the same soil kept for 4 or 4½ months in boxes; the stored soil had been kept in a damp and loose condition.

Addition of straw, glycerol, dextrose, and lactates, both separately and in mixtures, considerably diminished the yields in the first year. In the second year, straw was beneficial, whilst glycerol and sodium lactate had hardly any effect. Fresh stable manure had very little effect in the first year, but gave a decided increase in the second.

Inoculation with alinit was injurious, and in presence of straw and glycerol much more injurious. The effect of alinit was, however, very slight in the second year.

The injurious effect of the carbonaceous substances employed is attributed to the destruction of the small amount of nitrate formed in the soil. Glycerol, lactates, and dextrose are used up during the first year.

N. H. J. M.

Value of Nitrogen in Horn-meal as compared with Nitric Nitrogen. By MAX GERLACH (*Bied. Centr.*, 1901, 30, 450).—Oats and carrots were grown in loamy sand, containing N 0.110 per cent., manured with sodium nitrate, ammonium sulphate, and horn-meal respectively, in increasing amounts. There were two series of pots, one with, the other without, lime. All the pots received sufficient potash and phosphoric acid.

The results, which are given in a table, are inconclusive; the experiments are being continued.

N. H. J. M.

Analytical Chemistry.

Tables for the Calculation of Quantitative Analyses. By A. SARTORI (*Zeit. anal. Chem.*, 1901, 40, 201—376, and 5 pages of Supplement).—This elaborate table gives factors, both numerical and logarithmic (7 places of decimals), for the conversion of substance found into substance sought in upwards of 1100 cases. It is based on the atomic weights published in 1898 by the German Committee (*Ber.*, 31, 2761), in which oxygen = 16. M. J. S.

Value of the Correction for the Mercury Meniscus. By LUDWIG W. WINKLER (*Zeit. anal. Chem.*, 1901, 40, 403—404).—Glass tubes, with one end closed and the other ground flat, were fixed with the open ends upwards and filled with mercury. A plate of glass was then depressed upon the open ends of the tubes, and after its

removal the elevation of the meniscus above the edges of the tubes was measured with the cathetometer. For wide tubes (up to 25 mm. diameter), considerably higher values were obtained than those given by Bunsen. M. J. S.

New Form of Burette. By EDMUND THIELE (*Zeit. anal. Chem.*, 1901, 40, 405—406).—This burette is closed at its lower end, but has a hole in the side near that end. A glass cap, ending in a jet, and with an internal groove carried upwards from the jet as far as the hole, is ground to fit the end of the burette. By rotating either the cap or the burette itself, the groove is made to communicate with the hole. A side tube in the cap, opposite to the groove, communicates with the reservoir of standard solution, and allows the burette to be filled by rotating it through 180°. M. J. S.

Properties and Estimation of Alkali Persulphates. By B. MOREAU (*Chem. Centr.*, 1901, ii, 56—57; from *Apoth. Zeit.*, 1901, 16, 383).—A summary of the well-known properties of alkali persulphates. Two methods are recommended for the estimation of persulphates. (1) Five grams of potassium iodide are dissolved in 40 c.c. of water and 2 c.c. of sulphuric acid, water is added to make up to 50 c.c., 0.25 gram of the persulphate is added, and after 1 or 2 hours, the liberated iodine is estimated with *N*/10 sodium thiosulphate. Each c.c. of this represents 0.0135 gram of potassium, 0.0119 gram of sodium, or 0.0144 gram of ammonium persulphate.

(2) Two grams of potassium iodide and 2 grams of sodium hydrogen carbonate are dissolved in 50 c.c. of *N*/10 sodium arsenite, 0.25 gram of the persulphate is added, the whole heated just to boiling, and after 5 minutes, the liquid is again made up to 50 c.c. and titrated with *N*/10 iodine. The same calculation is applied. L. DE K.

Estimation of Ammonia in Urine. By OTTO FOLIN (*Zeit. physiol. Chem.*, 1901, 32, 515—517).—The urine is mixed with 400—500 c.c. of water, and then distilled for 45 minutes with magnesia or lime, and the ammonia collected in the usual manner in *N*/10 hydrochloric acid; the ammonia which passes over is the ammonia originally present in the urine, *plus* a certain amount due to the slow decomposition of urea. The amount of ammonia derived from the second source can be determined by making the residue in the flask up to its original volume, and distilling again for the same length of time. J. J. S.

Estimation of Phosphoric Acid as Ammonium Phosphomolybdate. By HENRI PELLET (*Anal. Chim. anal. appl.*, 1901, 6, 248—251).—A reply to Ledoux (*ibid.*, 224). The author refers to various publications by himself on the subject of the estimation of phosphoric acid as ammonium phosphomolybdate, results of which are now fully confirmed by Ledoux and several other chemists. The complete separation of the yellow compound in the cold requires a special shaking apparatus; on the whole, it is safer to heat the liquid in the water-bath. L. DE K.

Estimation of Phosphoric Acid in Phosphatic Manures, by Precipitation in the cold as Ammonium Phosphomolybdate. By L. LEDOUX (*Chem. Centr.*, 1901, i, 1341—1342; from *Bull. Assoc. Belge des Chimistes*, 1901, 15, 125—129).—The reagent is prepared by dissolving 150 grams of molybdic acid in 600 c.c. of ammonia of sp. gr. 0.96, and pouring this into 1070 c.c. of nitric acid of sp. gr. 1.22. To estimate the citrate-solubility, 2 grams of a superphosphate or 4 grams of a mixed phosphate are treated as usual with citrate solution, and the liquid is diluted to 250 c.c.; 50 c.c. are then boiled for 5 minutes with 15 c.c. of nitric acid of sp. gr. 1.40 to convert the phosphoric acid completely into the ortho-compound. When cold, 15 c.c. of ammonia of sp. gr. 0.92 are added, and then 100 c.c. of the molybdate solution, when the whole is stirred for 30 minutes by mechanical means at the rate of 250 times per minute. The precipitate may then be titrated according to Pemberton's directions, or dissolved in ammonia and precipitated with magnesia mixture. L. DE K.

Value of the Molybdate Process when estimating the Citrate-solubility of Basic Slag. By OTTO FOERSTER (*Chem. Zeit.*, 1901, 25, 421).—In order to obtain the "yellow precipitate" free from silica, the beaker containing the citrate solution of the phosphate and the molybdate reagent should be placed in the water-bath, heated to 80°, and kept there until cold. At a higher temperature, the precipitate will contain silicic acid. L. DE K.

Estimation of Phosphoric Acid in Soils by centrifugalising the Ammonium Phosphomolybdate. By EUGEN GULLY (*Chem. Zeit.*, 1901, 25, 419—421).—Von Jüptner's method for the rapid estimation of phosphorus in iron may be applied to soils. The hydrochloric acid solution of the soil is repeatedly evaporated with nitric acid to expel hydrochloric acid, and to render any silica insoluble. The residue is then dissolved in nitric acid of sp. gr. 1.19, and diluted to 50 c.c.; 25 c.c. of this solution are then introduced into a special calibrated apparatus, the graduated tube of which contains a 25 per cent. solution of ammonium nitrate, and heated for 10 minutes to 65°, when 25 c.c. of molybdate solution are added. After shaking for 1 minute, the apparatus is filled with the solution of ammonium nitrate, and then placed again for 20 minutes in the hot water, when it is taken out and whirled for 4 minutes in a centrifugal apparatus at 1100—1200 revolutions per minute. The volume of the precipitate is then read, and by means of a table the number of milligrams of phosphoric oxide corresponding with it is ascertained. When dealing with soils containing up to 0.184 per cent. of phosphoric oxide, 10 grams may be weighed; when richer samples have to be tested, a smaller quantity should be taken. L. DE K.

Gutzeit's Test for Arsenic. By F. C. J. BIRD (*Analyst*, 1901, 26, 181—187).—The author's apparatus consists essentially of a 150 c.c. flask, connected sideways with a long stemmed, bent top funnel holding 35 c.c. of hydrochloric acid. Seventy c.c. of the liquid to be tested for traces of arsenic, beer for instance, are introduced into the flask, 4 grams of pure zinc are added, and the whole is gently boiled

whilst the acid is gradually run in. The aqueous vapour is condensed in a bulb surrounded by cold water, and runs back into the flask. The hydrogen then enters a bulb into which an inverted funnel has been placed, and is washed by means of a 10 per cent. solution of lead acetate. After passing through a disc of lead acetate paper, the gas is made to act on two 5 mm. discs of mercuric chloride paper; a tube holding a disc of 20 mm. in diameter is also provided in case the amount of arsenic should be somewhat larger than expected. The discs will be coloured yellow or orange to orange-brown if the hydrogen contains arsenic hydride. The spots may be further identified by treating them with warm hydrochloric acid in which they are insoluble. After removal of the mercuric chloride, they may be dissolved in hydrochloric acid with the aid of a trace of bromine, and Bettendorff's stannous chloride test for arsenic may then be applied.

With care, it is quite possible to state positively whether the arsenic in the beer is below or exceeds a certain limit. L. DE K.

Arsenic Estimations relating to Malt Kilns. By THOMAS FAIRLEY (*Analyst*, 1901, 26, 177—180).—Owing to the use of fuel contaminated with arsenic, this substance gradually accumulates, particularly in the unglazed tiles of the malt kilns and in the dust from the walls, &c.

For the qualitative detection of arsenic in the tiles, 2—5 grams of the finely-powdered material are heated with 20—50 c.c. of a pure 25 per cent. sulphuric acid on the water-bath for 2 hours, the whole is then diluted to 50—100 c.c., and a measured portion tested in the Marsh apparatus; by comparison with a standard set of mirrors from known amounts of arsenic, an approximate estimation may be made. For the gravimetric estimations, 10—20 grams of the sample are distilled with hydrochloric acid and ferrous chloride. The arsenic is then precipitated in the distillate by hydrogen sulphide.

Dust is treated in a similar manner after heating 1—5 grams with 10—50 c.c. of sulphuric and 20 c.c. of nitric acid until the nitric acid is driven off; the cold liquid is diluted to 50—100 c.c., and a portion tested in Marsh's apparatus. For the quantitative estimation, 5 grams of dust are distilled with hydrochloric acid and ferrous chloride.

As much as 1 per cent. of arsenious acid has been found in the dust, and 0·12 per cent. in unglazed floor tiles. L. DE K.

Detection of Potassium by Sodium Picrate. By C. REICHARD (*Zeit. anal. Chem.*, 1901, 40, 377—384).—Potassium picrate being less soluble in water than the platinichloride, the use of a saturated (10 per cent) solution of sodium picrate is advocated as a reagent for potassium. A 1 per cent. solution of potassium chloride mixed with an excess of the reagent gives a precipitate of acicular crystals; weaker solutions yield no precipitate. Other potassium salts (except the carbonate and cyanide) must be of at least 2 per cent. strength to afford precipitates. The reaction is not interfered with by the presence of sodium salts (except the carbonate), but ammonium salts and free acids must be absent. The reaction is still more sensitive for caesium

rubidium, and thallium salts than for those of potassium; lithium salts, on the contrary, are not precipitated. M. J. S.

Estimation of Potassium. By O. SCHUMM (*Zeit. anal. Chem.*, 1901, 40, 385—389).—The platinichloride, instead of being weighed, may be dissolved and electrolysed. From a solution acidified with 1/50 of its volume of sulphuric acid (1:5) and kept at 55—65°, the platinum is completely deposited in a state resembling hammered platinum by a current of $ND.100=0.03$ ampere and 1.2 volts in 5—6 hours. The metal should be deposited on the inside of a platinum capsule. Employing Fresenius' method of precipitation, but washing with absolute instead of 80 per cent. alcohol, the factor 0.764595 was obtained for $2KCl/Pt$ with quantities of about 0.2 gram of potassium chloride; for quantities of 0.033 gram, the factor was 0.76689. M. J. S.

Estimation of Silver in Ores containing Sulphur. By AUGUSTE HOLLARD (*Ann. Chim. anal. appl.*, 1901, 6, 251—253).—One hundred grams of the finely powdered mineral (galena, for instance) are heated with 600 c.c. of water and 140 c.c. of nitric acid, and when practically dissolved, a few drops of a solution of lead chloride saturated at 80° are added, and the whole kept at that temperature for some time. The insoluble matter is collected on a filter and washed, and should it be suspected to contain much lead sulphate, this may be removed by means of aqueous sodium hydroxide of sp. gr. 1.1. The residue is now treated with 250 c.c. of a 2 per cent. solution of potassium cyanide which dissolves any silver chloride, and from the solution the metal is then deposited by electrolysis for a few hours, using a current of 0.05 ampere. The deposit may be weighed, but if it is very trifling (and the process is really intended for extremely poor ores) it is best estimated by dissolving it in nitric acid and titrating the solution with potassium thiocyanate, with iron alum as indicator.

The process may be also applied to crude copper. This is dissolved in a mixture of nitro-hydrochloric and sulphuric acids and evaporated nearly to dryness; the mass is then dissolved in dilute nitric acid containing a little hydrochloric acid, and the insoluble residue treated with potassium cyanide as previously directed. L. DE K.

Estimation of Calcium in high-grade Ferro-Silicon. By G. WATSON GRAY (*J. Soc. Chem. Ind.*, 1901, 20, 538—539).—A sample of ferro-silicon recently examined by the author contained as much as 3.29 per cent. of calcium in addition to small quantities of chromium, manganese, aluminium, magnesium, carbon, sulphur, phosphorus, tungsten, and traces of copper and nickel. So far as the author is aware, calcium has never been met with, as yet, in samples of ferro-silicon, although its presence may be explained by the fact that the flux used in its preparation is strongly calcareous.

Full details are given as to the best methods of testing for the various impurities. The alloy may be readily decomposed by hydrochloric acid after a preliminary fusion with sodium potassium carbonate. After separating the silica, calcium, &c., is estimated in the acid filtrate as usual. L. DE K.

Cement Testing. By OTTO H. KLEIN and STEPHEN F. PECKHAM (*J. Soc. Chem. Ind.*, 1901, 20, 539—544. Compare Abstr., 1900, ii, 627).—A criticism of the methods proposed for the chemical testing of hydraulic cement. Humphrey's method, which involves a preliminary fusion of the sample with sodium carbonate, is not suitable, as it also gives the silica from any undecomposed clay, which is, of course, worthless.

The sample for chemical analysis should be exactly like the one submitted to the physical tests, and should neither be dried nor powdered. Five grams should be treated in the cold with 250 c.c. of hydrochloric acid containing 10 per cent. of hydrogen chloride, and stirred at intervals for half an hour. Any residue should be collected and weighed, and further examined if necessary. The solution is now evaporated to render the silica insoluble, and the mass treated in the usual manner with hydrochloric acid. The silica thus obtained represents the soluble, or available, silica in the sample. Aluminium, iron, calcium and magnesium oxides, alkalis and sulphates, are estimated in the filtrate by the ordinary methods. Matter volatile at a red heat is estimated in another portion of the sample. L. DE K.

Estimation of Zinc by means of Iodine Solution. By PETER KNAPS (*Chem. Zeit.*, 1901, 25, 539—540).—Zinc may be accurately estimated by precipitation in acetic acid solution by means of hydrogen sulphide, removing the excess of this by boiling, and titrating the precipitate with excess of standard iodine and sodium thiosulphate. If, however, the solution contains more than 0.05 gram of zinc per 200 c.c., the zinc sulphide, owing to the separated sulphur, partly escapes the action of the iodine.

This inconvenience may be avoided by adding to the solution, previous to the precipitation of the zinc, 10—20 c.c. of a solution of 150 grams of crystallised barium chloride per litre, and the same quantity of a solution of 200 grams of crystallised sodium sulphate per litre; the precipitated barium sulphate then prevents the zinc sulphide from conglomerating. L. DE K.

Detection of Mercury in Urine. By BRUNO BARDACH (*Chem. Centr.*, 1901, ii, 1344; from *Centr. Bl. inn. Med.*, 22, 361—364).—Two hundred and fifty to 1000 c.c. of the urine are mixed with 0.8 gram of finely divided egg-albumin, 5—7 c.c. of 30 per cent. acetic acid are added, and the albumin precipitated by heating in the water-bath. The coagulum, which contains all the mercury, is collected and dissolved in 10 c.c. of hydrochloric acid of sp. gr. 1.19. This solution is then heated for 45 minutes with a clean copper spiral in the boiling water-bath. The spiral is washed with water, alcohol, and ether, carefully dried between filter-paper, and then heated in a long glass tube with a particle of iodine. If mercury is present, a yellowish or red ring will form on the colder part of the tube. L. DE K.

Estimation of Manganese in Ferro-Manganese and Nickel in Steel. By GEORGE L. NORRIS (*J. Soc. Chem. Ind.*, 1901, 20, 551).—*Estimation of Manganese in Ferro-Manganese.*—0.5 gram of the sample is dissolved in 15 c.c. of nitric acid of sp. gr. 1.42, and the

solution evaporated to dryness. The residue is dissolved in 30 c.c. of dilute hydrochloric acid (1:1), and introduced into a separating funnel. After adding a few drops of bromine and 40—50 c.c. of acetone, the liquid is shaken with 75 c.c. of ether, which dissolves the ferric chloride. The aqueous layer is removed and mixed with 300 c.c. of hot water to expel the bulk of the ether and acetone, the whole is brought to the boiling point, 5 grams of sodium acetate are added, and the manganese is precipitated as phosphate by adding 20 c.c. of a 10 per cent. solution of sodium ammonium phosphate and an excess of ammonia. After weighing the ignited precipitate, it may be tested in the usual way for traces of silica and iron, which, however, are as a rule practically absent; if chromium is present, this may be estimated by dissolving the precipitate in just sufficient hydrochloric acid, and reprecipitating the chromium as phosphate by addition of sodium acetate.

Estimation of Nickel in Steel.—One gram of steel is dissolved in 20 c.c. of nitric acid of sp. gr. 1.2, and the liquid evaporated to dryness, and then dissolved in 30 c.c. of dilute hydrochloric acid (1:1). After transferring it to a separating funnel, a few drops of bromine and 50 c.c. of acetone are added, and the whole is then shaken with 50 c.c. of ether; the aqueous layer is drawn off and shaken once more with 50 c.c. of ether. After adding 300 c.c. of hot water, and then boiling for a moment, 10 grams of sodium acetate and 10 c.c. of a 10 per cent. solution of sodium ammonium phosphate are added, the boiling is continued, and excess of ammonia is added. Any iron, manganese, chromium, or aluminium is precipitated as phosphate, whilst nickel and any copper remain in solution. The copper is removed by adding hydrochloric acid and passing hydrogen sulphide, and the nickel then precipitated in the filtrate by neutralising with ammonia and boiling. The nickel sulphide is finally converted into oxide by ignition, and weighed as such. L. DE K.

Potassium Thiocyanate as Indicator in the reduction of Ferric Salts. By JAKOB VOLHARD (*Zeit. angew. Chem.*, 1901, 14, 609—610).—The author rejects as perfectly untrustworthy the process recommended by Ebeling (this vol., ii, 424). Potassium thiocyanate is gradually reduced by nascent hydrogen, and then no longer indicates the presence of ferric iron; the result obtained by titration with permanganate may, therefore, be too low; on the other hand, if after complete reduction of the iron, any thiocyanate is left, this will consume some permanganate and the result will be too high. L. DE K.

Detection of Tin. By OTTO SCHMATOLLA (*Chem. Zeit.*, 1901, 25, 468).—If a porcelain or glass rod, or, better still, a narrow test-tube containing water, is dipped into a solution of tin in hydrochloric acid, and then held in a colourless bunsen flame, an intensely white flame is noticed, which persists until the hydrogen chloride is driven off. Antimony does not interfere with the reaction, but an excess of arsenic prevents it; a dark deposit of tin arsenide then forms on the glass. Curiously enough, the test does not succeed with platinum wire. As it is a very delicate one, it will no doubt be found useful in the analysis of tinned foods. L. DE K.

Reaction characteristic of Pure Waters. By HENRI CAUSSE (*Compt. rend.*, 1901, 133, 71—74).—If a solution of 0.25 gram of crystal violet (hexamethyltriaminotriphenylcarbinol) in 25 c.c. of a cold saturated solution of sulphur dioxide is added in small quantity (1.5 c.c. to 100 c.c.) to pure water, the violet colour is restored, the intensity of the coloration being much greater if the water has been heated at 35—40° for two hours, and afterwards cooled before adding the reagent. All pure natural waters give this reaction, but if the water is contaminated with sewage or sewage effluent there is no production of colour, probably owing to the presence of sulphur compounds.

Where the new reagent gives a positive reaction, sodium *p*-diazobenzenesulphonate and magenta and sulphurous acid respectively give negative reactions, and *vice versa*. By means of the reagent, it was found possible to trace the appearance of sewage in the Rhone as the result of rain storms, and its gradual disappearance after the storms had ceased.

C. H. B.

Technical Analysis and Softening of Feed-water for Boilers. By GIOVANNI GIORGIS and G. FELICIANI (*Gazzetta*, 1901, 31, i, 416—425).—A reply to criticisms on the authors' methods (*Abstr.*, 1899, ii, 453) made by Gianoli in a communication to the Chemical Society of Milan (see *L'Industria*, 1899, 13, 346—348). T. H. P.

The isoPurpuric Acid Reaction for Cyanides. By C. REICHARD (*Chem. Zeit.*, 1901, 25, 537—538, 555—556).—The author states that the well-known picric acid test for cyanides must be restricted to solutions of alkali cyanides. The solution should be moderately alkaline, and instead of picric acid its sodium salt should be used. Although warming accelerates the reaction, it is best to use cold solutions.

Insoluble cyanides when heated with solution of sodium picrate do not give the reaction. In a few instances, the test has more or less succeeded after heating the cyanide with solution of sodium hydroxide or with water and barium dioxide, but the reaction then becomes rather complicated.

L. DE K.

Detection of Methyl Alcohol in the Presence of Ethyl Alcohol. By ALBERT B. PRESCOTT (*Pharm. Arch.*, 1901, 4, 86—90).—One c.c. of the sample, or enough to represent 1 c.c. of absolute alcohol, is put into a test-tube 16 mm. wide and 16 cm. long, and 8 c.c. of water are added. A copper coil, made from wire 1 mm. thick, and wound over a rod 7—8 mm. thick (and over the other end of the wire) to make a close coil 3—3.5 cm. long, with a stem of two twisted wires about 20 c.c. long and bent at right angles about 6 cm. from the free end, is heated in the upper part of a bunsen flame to a red heat, and plunged steadily to the bottom of the liquid for a second; this operation is repeated 4 or 6 times until the coil no longer turns bright. Six c.c. of a 3 per cent. solution of hydrogen peroxide are added to remove the acetaldehyde, and the liquid is filtered into a porcelain dish. After 3 minutes, 2 c.c. of a solution of sodium thio-sulphate (1 : 10) are added to remove the excess of hydrogen peroxide

and the liquid is then tested for formaldehyde by means of phloroglucinol. One gram of this is dissolved in 90 c.c. of water, 20 grams of sodium hydroxide are added, and the whole diluted to 100 c.c.; 3 c.c. of this solution are added to the contents of the dish. If formaldehyde is present, a bright red colour (not a purple) will at once make its appearance, but unless it is very intense it will again rapidly fade. The presence of formaldehyde proves, of course, the presence of methyl alcohol in the spirit. L. DE K.

New Method for identifying Renatured Spirits. By P. N. RAIKOW and P. SCHARBANOFF (*Chem. Zeit.*, 1901, 25, 434—436).—As it is possible to remove the pyridine bases but not the methyl alcohol from denatured spirit, the authors identify renatured spirit by the presence of methyl alcohol, and this is easily recognised by converting it into formaldehyde. The spirit is first rendered absolute by means of anhydrous potassium carbonate, and 10—20 c.c. are then put into a 100 c.c. Erlenmeyer flask and at first gently warmed. Inside the flask, and close to the liquid, is then suspended a red hot platinum spiral of 0.3 mm. in thickness; thinner wire should not be used as the oxidation then proceeds in too violent a manner, and even pure ethyl alcohol would yield formaldehyde.

In the presence of methyl alcohol, formaldehyde is gradually formed and easily recognised by its odour. To detect the formaldehyde with certainty, the air escaping from the flask should be drawn by means of an aspirator through water contained in a test-tube; formaldehyde is dissolved in the water, whilst most of the acetaldehyde is carried away by the current of air. The presence of formaldehyde in the water may then be recognised both by the odour and other reactions. L. DE K.

Estimation of Foreign Volatile Components of Explosives containing Nitroglycerol. By LOUIS W. DUPRÉ (*Chem. Zeit.*, 1901, 25, 540).—About 2 grams of the sample are dried for one hour in a watch glass placed on a copper water-bath not provided with holes. To prevent volatilisation of nitroglycerol, a tall, narrow beaker, which is weighed together with the watch glass, is placed over the latter; any fumes of nitroglycerol are condensed on the inner surface of the glass, but water-vapour is carried off by the air currents. The process is stated to have been found satisfactory in practice. L. DE K.

Estimation of Minute Amounts of Sugar in Urine. By EMIL RAIMANN (*Zeit. anal. Chem.*, 1901, 40, 390—402).—An attempt to employ the process of Laves (*Abstr.*, 1893, ii, 555) for the estimation of sugar in normal urine showed that although concordant results were obtained, it was impossible to regard them as even approximately true. A large proportion of the precipitate is derived from substances other than sugar present in the urine, and an amount, varying according to circumstances, from the phenylhydrazine itself. The only method which gave satisfactory results was to take two portions of the sample of urine, free one of them completely from sugar by fermentation for 24 hours at 34° with yeast, precipitate both with phenylhydrazine, and estimate the sugar from the difference. Ex-

periments in which dextrose was added to a fermented urine, and the solution so obtained was analysed by this differential method, showed that the yield of osazone is only 49 per cent. of the calculated amount, and that the results did not vary more than 6 per cent. from the mean, even when the amount of sugar was as small as 0.04 gram per litre.

M. J. S.

Estimation of Sugar in Swedes. By SYDNEY HOARE COLLINS (*J. Soc. Chem. Ind.*, 1901, 20, 536—538).—The process is based on the estimation, by a colorimetric method, of the copper left in solution after heating the Fehling solution with sugar.

Ten grams of swedes, 100 c.c. of water, and 1 c.c. of a saturated solution of lead acetate are ground up together in a mortar and left for some hours. Fifty c.c. of the filtrate are put into a test-tube, 0.5 c.c. of sulphuric acid is added, and the liquid heated in a steamer for 20 minutes. When cold, 4 c.c. of the supernatant liquid are pipetted off, and mixed in a test-tube with 10 c.c. of freshly prepared Fehling solution of half the usual strength. The author has found that, in the circumstances, 10 c.c. of this Fehling solution represent 0.0216 gram of invert sugar, and this figure is used in the analysis of swedes. After replacing the tube in the steamer for 30 minutes, the cuprous oxide will have completely settled, and the colour of the liquid is now compared with a series of standard tints. These standards contain 0.125, 0.25, 0.375, 3.50, 0.625, 0.750, 0.875, and 1 c.c. respectively of Fehling's copper sulphate solution; to each is then added 2.5 c.c. of Fehling's alkaline tartrate solution, and the liquid is diluted to 14 c.c. Having thus ascertained how much copper solution has escaped reduction, the calculation of the percentage of sugar in the sample is an easy matter. When dealing with dried swedes, a yellow colour is imparted to the solutions, causing various shades of greenish-blue which cannot be well compared with the standards. In this case, the author uses a special colorimeter. On one pane of glass, a row of test-tubes containing alternately plain water and a graduated series of yellow solutions is placed; on another pane, a row of tubes containing the standard blue solutions is placed over the yellow tubes, blank spaces being left over the plain tubes to take the tubes used for the actual analysis. The pane holding the blue tints slides over the pane holding the yellow tints, producing any desired combination, and the whole is placed in a wooden frame at an angle of 45° with a white base board. Methyl-orange is a suitable material for making the yellow solutions.

Attention is called to the unequal distribution of the saccharine matter in a swede.

L. DE K.

Testing Flour. By ALEXANDER ZEGA (*Chem. Zeit.*, 1901, 25, 540—541. Compare Abstr., 1900, ii, 503).—The reagent is prepared by diluting 3 c.c. of a concentrated solution of magenta in alcohol with water to 200 c.c. and passing sulphur dioxide until the liquid is completely decolorised; before use, this is diluted with water in the proportion of 1 to 10, and 1 c.c. of this solution should require for neutralisation 0.8 c.c. of *N*/10 alkali. To apply the test to flour, 1 gram of the sample (this may be measured) is put into a test-tube

and shaken with 10 c.c. of water and 1 c.c. of the reagent. When dealing with samples rich in bran, 1.5 or 2 c.c. should be added. Pure fresh flour remains colourless for 2 or 3 minutes, but when it is mouldy, or when it contains an undue excess of bran, it assumes a more or less intense red colour.

L. DE K.

Evaluation of Gum Arabic. By KARL DIETERICH (*Zeit. anal. Chem.*, 1901, 40, 408—410).—In connection with the researches of Fromm (this vol., ii, 426), the author states that he published in 1896 and 1897, in Helfenberger's *Annalen*, the results of acidity estimations in samples of gum arabic, and showed that direct titration by alkali always gave low results. The method he employed was to place 1 gram of the finely powdered gum in a mixture of 10 c.c. of $N/2$ aqueous, and 10 c.c. of $N/2$ alcoholic potassium hydroxide, and after 24 hours to titrate back with $N/2$ sulphuric acid. If either of the alkali solutions was used exclusively, the results were lower. Gum arabic consists chiefly of acid calcium salts, and it would seem that the conversion of these into normal salts is gradual.

M. J. S.

Analysis of Commercial Cream of Tartar. By HENRI QUANTIN (*Ann. Chim. anal. appl.*, 1901, 6, 244—248).—The total acidity of the sample is determined as usual; from this is deducted the acidity due to foreign acids, and the difference is calculated to potassium hydrogen tartrate. The acidity due to acids other than tartaric is estimated by recrystallising a known weight of the sample from boiling water and allowing to cool; an aliquot part of the filtrate is then titrated, allowance being made for the amount of potassium hydrogen tartrate which at a definite temperature is retained by the mother liquor.

The test may also be made as follows. One to two grams of the sample are treated with 25 c.c. of boiling water, and when cold a sufficiency of alcohol is added. The insoluble matter is then collected on a filter, washed with alcohol to remove the foreign acids, and the filter having been returned to the beaker, the mass is boiled with water and titrated.

When dealing with crude tartars the approaching end of the titration is generally shown by a change of colour of the solution; towards the finish, delicate litmus paper should be used.

L. DE K.

Analysis and Composition of Lemon Juices. By EDUARD SPAETH (*Zeit. Nahr.-Genussm.*, 1901, 4, 529—541).—Adulteration of lemon juice with water and citric acid may be detected by the diminished amount of ash, and by its alkalinity; 100 c.c. of normal juice yield from 0.374 to 0.455 gram of ash, and this requires for neutralisation 4 to 6 c.c. of N acid.

Adulteration with tartaric acid is best detected as follows: 10 c.c. of the sample are diluted to 50 c.c., and mixed with 50 c.c. of alcohol and 5—10 c.c. of basic lead acetate. The precipitate, which contains the organic acids as lead salts, is washed with dilute alcohol, then suspended in water, and decomposed with hydrogen sulphide; the lead sulphide is washed with hot water, and the filtrate concentrated to 10 c.c. This is neutralised with N alkali, and then mixed with 2.5 c.c.

of glacial acetic acid, 2 c.c. of a 20 per cent. solution of potassium acetate, and 40 c.c. of a 20—25 per cent. solution of potassium chloride. The whole is well stirred and 50 c.c. of 96 per cent. alcohol are added. After 12—18 hours, the separated potassium hydrogen tartrate is collected on a filter, washed first with dilute and then with absolute alcohol, dissolved in boiling water, and titrated with *N* alkali.

Other analytical processes are discussed, and several tables are given. As regards lemon-syrup, 100 c.c. of this should contain about 0.14 gram of ash, requiring 1.7 c.c. of *N* acid for neutralisation.

L. DE K.

Estimation of Uric Acid in Urine. By OTTO FOLIN and PHIL A. SHAFFER (*Zeit. physiol. Chem.*, 1901, 32, 552—572. Compare Abstr., 1898, ii, 196, 465; Wörner, 1900, ii, 251; Jolles, 1900, ii, 450).—In Salkowski's method for estimating uric acid it is advisable to precipitate the silver magnesium urate and phosphate together as recommended by Ludwig, as otherwise a small amount of urate (2 mg. per 100 c.c.) is lost during the precipitation of phosphates. The silver magnesium urate is then decomposed by hydrogen sulphide in acid solution and in order to precipitate readily all the silver it is advisable to add 5—10 c.c. of a 1 per cent. copper sulphate solution and boil. It is always necessary to make a correction for the solubility of uric acid, but the actual amount appears to vary in different cases.

The ammonium sulphate method has been somewhat altered as follows. A solution containing ammonium sulphate, 500 grams, uranium acetate, 5 grams, and 10 per cent. acetic acid, 60 c.c. per litre is prepared and 75 c.c. of this solution are mixed with 300 c.c. of the urine, kept for 5 minutes, passed through a double filter, and two quantities of 125 c.c. each collected. Five c.c. of concentrated ammonia are added to each and they are allowed to remain overnight, then filtered and the ammonium urate estimated as in the original method. The addition of uranium acetate is made in order to precipitate a minute quantity of mucoid substance which is otherwise thrown down on the addition of ammonia. As this also reduces permanganate, it accounts for the fact that the numbers previously found by the author and also by Jolles are too high. A correction of 3 mg. uric acid per 100 c.c. should always be made on account of the solubility of ammonium urate. The methods of Mörner and of Jolles are adversely criticised.

J. J. S.

Sensibility of the Methods for the Detection of Salicylic Acid in Wines. By ANTONIO J. FERREIRA DA SILVA (*Rev. Intern. Falsific.*, 1901, 14, 68—70).—A table showing the comparative delicacy of the chief methods in use for the detection of salicylic acid in wines.

The method in use in the municipal laboratory in Paris, extraction with ether and purification of the extract with benzene, shows 1 part of the acid in 33,000 parts. Weigert-Rösler's method, extraction with chloroform or carbon disulphide, shows 1 part in 100,000. The original official German method, extraction with a mixture of ether and light petroleum, shows 1 part in 200,000; the modified process, purifying the residue by means of benzene, instead of a mixture of ether and light petroleum, shows 1 part in 100,000 only.

L. DE K.

New Fat Extraction Apparatus. By W. JERWITZ (*Chem. News*, 1901, 83, 229).—The apparatus will be readily understood from the accompanying figure. It is also supplied with two specially constructed clamps, which may be fastened to a

wooden partition or to a board fixed to the wall; these clamps, which give a safe, but not absolutely rigid, grip, allow the apparatus to be rotated on its long axis, and it need not again be taken from its stand when it has been once fixed.

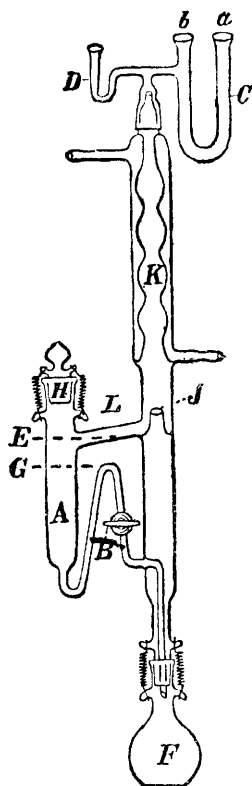
The flask, *F*, is attached to the bottom end of the apparatus with an ungreased joint by means of spiral springs. The cartridge, which contains the material to be extracted, is placed in *A*, and after closing the stopcock, *B*, the extractor is filled up to *E* with anhydrous ether. After inserting the glass stopper, *H*, which for safety is also held by two spiral springs, the cock is opened at *B*, and the ether saturated with fat flows from *A* into *F*.

The flask, *F*, which has no external support, is now heated in a water-bath, the temperature of which is kept constant. The ether distils off through *J* into the condenser, *K*, and is condensed; it is prevented from flowing back through *J* into *F*, but flows through *L* into *A*, where it again acts on the cartridge, and presently flows off into *F*.

When the extraction is complete, *B* is closed again, and the ether collects in *A*. When it has all distilled over, *F* is removed, and the ether is allowed to flow through *B* into another vessel; the cartridge is then removed with a pair of tongs.

The condenser is connected with two U-tubes; the larger one, *C*, containing calcium chloride, is closed at *a* by a stopper of wadding, but is made air-tight at *b*. *D* contains a mercury trap in case the calcium chloride tube should become choked, and acts as a safety valve.

L. DE K.



Apparatus for Estimating Fat. By HOMER J. WHEELER and BURT L. HARTWELL (*J. Amer. Chem. Soc.*, 1901, 23, 338—347).—An improvement on the well-known Knorr apparatus. The improvements may be summarised as follows. The flask is inexpensive and may be readily cleaned, and is connected with the extractor by means of a rubber cup which carries the requisite amount of mercury for sealing. The amount of ether which can collect around the outside of the neck of the flask is reduced to a minimum by adjusting the cup to any point of the neck. The end of the tube from which the condensed ether drops upon the substance is bent, so that the ether will be delivered from the centre and not flow down the glass. By a special

arrangement, extraction tubes or thimbles of different lengths may be used, and the ether collected without much loss in one receptacle after the end of the extraction without disconnecting the apparatus, and the ether is, moreover, maintained in a dry condition. For full details of the apparatus, which may be used either singly or in battery form, the original article and drawings should be consulted. L. DE K.

Hübl's Iodine Solution. By MORIZ KITT (*Chem. Zeit.*, 1901, 25, 540).—The author states that Hübl's solution may be rendered more stable by boiling it for 1 hour in a reflux apparatus. It then loses about two-thirds of its available iodine, but the resulting liquid does not undergo further decomposition in the cold for about 8 days.

L. DE K.

The Maumené Test for Oils. By C. AINSWORTH MITCHELL (*Analyst*, 1901, 26, 169—175).—The author has modified Maumené's process so as to render it suitable for oils which develop too much heat on adding sulphuric acid. Two grams of the oil are weighed into a vacuum jacketed tube (*Abstr.*, 1895, ii, 427), 10 grams of carbon tetrachloride are added, and then 2 c.c. of sulphuric acid. The mixture is stirred with a delicate thermometer and the rise in temperature noticed. The rise depends greatly on the strength of the acid, and even when using a 98 per cent. acid the results with unoxidised linseed oils are too low. The fatty acids of 25 different oils were treated with 93.8 per cent. acid, and the rise in temperature is tabulated. This rise, multiplied by 7, gives figures agreeing fairly well with the iodine figures of the fatty acids. The table also shows the thermal rise with bromine and the corresponding iodine value obtained by multiplying by 6.

A similar table is given for the fats themselves. When using 93.8 per cent. acid, the factor for the conversion into the iodine figure is 6.35; when using a 97.8 per cent. acid it is 4.3. The article may be summarised as follows: The Maumené figures obtained by the author's process are in direct proportion to the bromine thermal value of the fatty acids of most unoxidised oils, excepting castor oil, butter, and animal fats rendered at a high temperature. This relationship also applies, although in a less degree, to the glycerides. L. DE K.

Influence of the Season and Feeding on the Reichert-Meissl Number of Dutch Butter. By A. J. SWAVING (*Zeit. Nahr.-Genussm.*, 1901, 4, 577—585).—A very elaborate investigation as to the amount of volatile fatty acids contained in Dutch butter, which from natural causes may occasionally give a somewhat low Reichert-Meissl figure. It is noticed that this is generally accompanied by an increased "Crismer" number.

L. DE K.

A New Reaction of Acetone. By MAXIMILIAN STERNBERG (*Chem. Centr.*, 1901, i, 1270; from *Centr. Physiol.*, 25, 69—70).—Solutions of acetone, slightly acidified with phosphoric acid and treated with copper sulphate and iodine dissolved in potassium iodide, give, on warming, an abundant greyish-white precipitate. The reaction is very sensitive, although less so than that of Lieben. Alcohol only

gives the reaction on long boiling; acetophenone, benzaldehyde, and similar compounds do not produce it. Normal urine, free from acetone, gives a similar reaction, but acetone in urine may be detected by employing the distillate. M. J. S.

New Method of Testing "Saccharin." By CARL GLÜCKSMANN (*Chem. Centr.*, 1901, ii, 58—59; from *Pharm. Post*, 1901, 34, 234).—The chief impurity of commercial "saccharin" is *p*-sulphaminobenzoic acid, which has no sweetening power, and may occur to the extent of 40 per cent. In the absence of other impurities, the amount of true "saccharin" may be estimated by taking advantage of the difference in the molecular weight of those two substances; 1 gram of "saccharin" requires for neutralisation 54.6, and 1 gram of *p*-sulphaminobenzoic acid 49.7 c.c. of *N*/10 sodium hydroxide. Three to 5 grams of the suspected sample are dissolved in 90—150 c.c. of alcohol and titrated, with phenolphthalein as indicator. From the amount of sodium hydroxide consumed, the relative proportion of "saccharin" and the adulterant is easily calculated. L. DE K.

Estimation of "Saccharin" in Alimentary Substances. By H. DÉFOURNEL (*J. Pharm.*, 1901, [vi], 13, 512—515).—The methods of Allen and of Girard for the detection of "saccharin" are not well adapted for its quantitative estimation. "Saccharin," however, when treated in the cold with ammonia, yields the compound $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO} \\ \text{SO}_2\end{smallmatrix}\right\rangle\text{N}\cdot\text{NH}_4$, which, like other ammonium compounds, is decomposed by sodium hypobromite with liberation of nitrogen. The liquid to be analysed (250 c.c.) is therefore strongly acidified with 10 per cent. sulphuric acid, and shaken three times with 50 c.c. of a mixture of equal parts of ether and light petroleum. The ether-petroleum extract is thoroughly washed with water to remove acids, and then evaporated. The residue is treated with ammonia, the excess of which is expelled by heating on the water-bath. It is then dissolved in a few c.c. of water, and the solution decomposed by hypobromite in an ureometer. The number of c.c. of nitrogen divided by 0.89 gives the weight of "saccharin" in centigrams. M. J. S.

Composition of Jellies and Jams. By L. M. TOLMAN, L. S. MUNSON, and W. D. BIGELOW (*J. Amer. Chem. Soc.*, 1901, 23, 347—353).—Tables are given showing the results of the analyses of a large number of fruits and their juices, also of the jams and jellies prepared from them in the ordinary way. The analysis is restricted to total solids, ash, total acidity expressed as sulphuric acid, proteids, reducing sugars, sucrose, and also the polarisations before inversion at 18°, and after inversion both at 18° and at 86°. The rate of inversion of the added sucrose is not only influenced by the amount of free organic acid and time of boiling, but also by the nature of the organic acid. L. DE K.

General and Physical Chemistry.

Radio-activity of Salts of Radium. By P. CURIE and A. DEBIERNE (*Compt. rend.*, 1901, 133, 276—279).—Radio-activity may be communicated to distilled water by (1) distillation of a solution of radium chloride which has been allowed to stand several days; (2) placing a solution of a radium salt and distilled water in separate dishes in a perfectly closed space, (3) immersing in distilled water a celluloid capsule containing a solution of a radium salt. Such water may exhibit greater radio-activity than the substance from which it was prepared, but loses its power rapidly in an open vessel, and in the space of a few days if the vessel is kept closed. A solution of a radium salt also soon loses its activity in the open air, but regains it if transferred to a sealed tube. The author therefore considers that the radio-active energy may be transmitted by radiation, and also by a kind of conduction, whereby it passes from place to place by means of a gas or liquid, but not ordinarily through solids. A solution of a radium salt is hence in a state of equilibrium, and in a sealed tube, the loss of activity by radiation being slight, the value of the activity is high, but in an open vessel, the loss by conduction being considerable, the activity is very feeble.
L. M. J.

Electromotive Efficiency of the Elementary Gases. II. By EMIL BOSE (*Zeit. physikal. Chem.*, 1901, 38, 1—27. Compare Abstr., 1900, ii, 704).—The author concluded from his earlier work (*loc. cit.*) that the *E.M.F.* of Grove's gas cell has a higher value than is usually assigned to it. Besides the confirmation of this in Wilmshire's investigation (this vol., ii, 2), the author has himself found the value 1.1242 volts as a lower limit for the *E.M.F.* If the electrodes are polarised for a lengthened period with small current density so that they become super-charged with the gases, a series of determinations made as the cell depolarises reveals an upper limit value for the *E.M.F.*, namely, 1.1542 volts. The length of time required to effect this super-saturation shows that the ordinary charging of such electrodes can be merely superficial.

At the oxygen electrode of the Grove cell there is equilibrium between water, oxygen, and hydrogen peroxide. To this hydrogen peroxide, if its concentration be high enough, there corresponds a higher oxidation potential than that of oxygen under atmospheric pressure; the addition of ordinary hydrogen peroxide, however, to the electrolyte at an oxygen electrode lowers the potential, as observed by Glaser (Abstr., 1899, ii, 78), and Wilmshire (*loc. cit.*). When the hydrogen peroxide equilibrium just referred to has been established, rise of temperature lowers the potential to a value less than that for oxygen alone; this corresponds probably with the conversion of one hydrogen peroxide modification into another. So long as the theory

of the gas cell deals only with states of equilibrium, it need not be modified on account of the part played by the hydrogen peroxide.

J. C. P.

Electromotive Efficiency of the Elementary Gases. III. Observations relative to a new Electrode Sensitive to Light. By EMIL BOSE & HANS KOCHAN (*Zeit. physikal. Chem.*, 1901, 38, 28—55. Compare preceding abstract, and Bose, Abstr., 1900, ii, 704).—A cell with gold electrodes and sulphuric acid as electrolyte was polarised for seventeen days. During the process, the cathode became coated with a brownish deposit like finely divided gold, whilst on the anode an orange-coloured skin appeared, gradually becoming more powdery and falling to the bottom of the vessel. When the cell was left to itself, it was found that the *E.M.F.* showed remarkable periodic variations, being higher in the dark than in the light, and when it was kept entirely in the dark, the variations ceased. Experiments with an arc lamp showed that the oxygen electrode was the sensitive one. Daylight, electric light, magnesium light, and the light from an incandescent gas lamp all lower the oxidation potential at the anode; violet light has the same effect, but red light raises the potential; sodium light has practically no effect. The *E.M.F.* varies to the extent of 0.1 volt, according to the nature of the light. J. C. P.

Polarisation of Magnesium in Alkaline Solutions. By ADOLFO CAMPETTI (*Atti Accad. Sci. Torino*, 1900—1901, 36, 427—432).—When employed as anode in an electrolytic cell containing sodium or potassium hydroxide solution, magnesium shows a behaviour similar to that already noticed for aluminium (compare Graetz, Abstr., 1898, ii, 10), a great decrease in the current being produced, probably owing to the formation of a film of oxide on the surface of the aluminium.

T. H. P.

Electrolysis of Molten Lead Iodide and Lead Chloride with particular Reference to the Application of Faraday's Law and the Theory of the Electrolysis of Molten Salts. By GUSTAV AUERBACH (*Zeit. anorg. Chem.*, 1901, 28, 1—44).—Fused lead iodide at temperatures varying from 440° to 800° was electrolysed by a current of 24 volts and 1 to 2 amperes. The amount of lead separated at the lowest temperature was only about 90 per cent. of that which the current should form, and varied greatly in different experiments. As the temperature rises, the yield becomes smaller. Faraday assumed that during the course of the electrolysis, lead tetraiodide, PbI_4 , was formed, but the author finds no evidence in favour of this view.

In the electrolysis of lead chloride also, the quantity of lead separated falls short of the possible amount. Determination of the quantity of chlorine formed proves conclusively that the carbon electrodes (and to a slight extent the undecomposed salt) absorb chlorine, and consequently the evolution of chlorine depends on the duration of the electrolysis. After the process has gone on for some time and the carbon has become saturated, the quantity of chlorine liberated is nearly exactly (above 99 per cent.) equal to the amount required by Faraday's law.

This is the first time that Faraday's law has been proved for the *anode* in the case of a molten salt.

Lorenz (*Zeit. anorg. Chem.*, 1900, 23, 97) has suggested that the formula $\alpha = 100. \epsilon' / \epsilon$ represents the yield of the current (α), where ϵ is the polarisation of the molten salt, and ϵ' the depolarised value of the same. During the above experiments, the polarisation was also determined, and it has been found that Lorenz's formula, although not rigorously exact, gives approximate values.

When the lead chloride is mixed with lead oxide, the yield is precisely the same as when fused lead chloride alone is used, but no chlorine or oxygen is evolved.

During the electrolysis, a metallic "cloud" is given off from the cathode, and spreads through the fused mass. As it comes near the anode, it combines with the free chlorine there, and in this way gives rise to the irregularities in the amount of metal deposited, since the amount dissipated as "cloud" must vary greatly, with slight modifications of external circumstances. The "cloud" was examined by Tyndall's method, and it was proved that it is not formed of solid particles but is a true solution of the metal in the fused salt, which fact is confirmed by the circumstance that metallic cadmium may be crystallised from its fused chloride. J. McC.

Electrolytic Short Circuits in Liquid Cells. By OTTO SACKUR (*Zeit. Elektrochem.*, 1901, 7, 781—784).—The author has measured the *E.M.F.* of concentration cells containing electrodes of silver covered with silver chloride immersed in solutions containing different quantities of the chloride, and the same quantities of the nitrate of a metal. Potassium, lithium, and hydrogen salts are used. The *E.M.F.* of such a cell is made up of three single *P.D.*; the values of the two existing between the electrodes and the solutions depend only on the concentrations of the chlorine ions in the solutions. The difference between the *E.M.F.* of two cells containing salts of different metals, but having the same concentrations with respect to chlorine ions, is therefore due to the difference of the *P.D.* at the junctions of the solutions.

The values of these *P.D.* may be calculated from Nernst's theory (Abegg and Bose, *Zeit. physikal. Chem.*, 1899, 30, 545). The results of the author's experiments are in good agreement with those calculated from the theoretical formula. T. E.

Dissociation of Strong Electrolytes. By OTTO SACKUR (*Zeit. Elektrochem.*, 1901, 7, 784—787).—Jahn's view that the deviation of strong electrolytes from the dilution law is due to changes of ionic mobility with concentration is discussed. By means of Jahn's values for these mobilities (*Zeit. physikal. Chem.*, 1900, 35, 9), the author calculates the conductivities of solutions containing equal quantities of hydrochloric acid and potassium chloride, and of sodium and potassium chlorides, and finds that the calculated conductivity is 2 to 3 per cent. larger than that found. He is therefore of opinion that Jahn's conclusions are erroneous. Jahn has, however, already withdrawn them (*ibid.*, 1901, 37, 490). T. E.

[Degree of Dissociation and Dissociation Equilibrium in the case of Highly Dissociated Electrolytes.] A Correction. By HANS JAHN (*Zeit. physikal. Chem.*, 1901, 38, 125—126).—In regard to the new dissociation isotherm deduced in his recent paper (this vol., ii, 491), the author, whilst holding to the correctness of his theoretical treatment, acknowledges that the numerical data employed to test the theory are quite useless; it is not admissible to explain deviations from the simple gas laws with the help of numbers obtained on the hypothesis that these laws are valid. There is at present no satisfactory method of determining the ionic concentration in cases where the gas laws do not hold. J. C. P.

Electro-capillary Action of Non-dissociated Molecules. By A. GOUY (*Compt. rend.*, 1901, 133, 284—287).—An extension of the previous paper (this vol., ii, 435); curves are given for $E.M.F.$ against h (where h is the height of the electro-capillary column), in the case of a solution of sodium sulphate, and of the same solution with the addition of the organic compound. The effect of the latter is in all cases to cause a depression of h , most marked towards the middle of the curve, and becoming *nil* at the extremities. In this, the organic compounds differ from electrolytes, and hence, also, active molecules from active ions, as the latter cause a depression which increases from the positive side. The curves obtained with organic compounds, however, fall into certain groups, the discussion of which is deferred.

L. M. J.

Calculation of Heats of Dilution, according to Kirchhoff's Formula. By FERENCZ JÜTTNER (*Zeit. physikal. Chem.*, 1901, 38, 76—118).—In a review of the work done on this subject, and on the relation between theory and von Babo's law, the author points out that only in one case (Ewan and Ormandy, *Trans.*, 1892, 61, 769) has the calculation of heats of dilution by Kirchhoff's formula been successfully carried out. The calculation involves the expression $\log_e(P_0/P)$, where P_0 and P are the vapour pressures of solvent and solution, respectively, at the same temperature. Instead of direct vapour pressure determinations, the author uses published data regarding freezing and boiling points, and from these, calculates the values of the above expression. The solvents dealt with are water, benzene, and glacial acetic acid. Only for aqueous solutions of potassium chloride and nitrate—cases where the experimental data are exact and complete, and where the heat of dilution does not change its sign between 0° and 100° —was there quantitative agreement between the values of the heat of dilution calculated for the mean temperature of 50° and those obtained by experiment. In other cases, a qualitative agreement was found, but as a general rule, the experimental data are very defective. The author himself has determined the boiling points of aqueous solutions of sucrose, dextrose, lævulose, citric acid, and tartaric acid over a large range of concentration. J. C. P.

Latent Heat of Evaporation of Steam from Saturated Salt Solutions. By FREDERICK T. TROUTON (*Trans. Roy. Irish Acad.*, 1900, 31, 345—362).—With an apparatus similar to that used by

Marshall and Ramsay (*Phil. Mag.*, 1896, 41, 38), the author has determined the latent heat of evaporation of steam from saturated solutions of sodium nitrate, sodium sulphate, and calcium chloride. The two former boil at 121° and 103.5° respectively, and the values of the latent heat are 478.3 and 529; these salts dissolve with absorption of heat, hence the latent heat is less than in the case of pure water. Calcium chloride is of the opposite type, dissolving with development of heat; as it does not give a solution of maximum boiling point, three different solutions were used, boiling at 140° , 120° , and 103° respectively; the values of the latent heat obtained were 683, 606, and 545; these values point to the latent heat being a linear function of the temperature. The relation between the latent heat of evaporation and the heat of solution in the case of sodium nitrate has been calculated by means of a thermodynamic cycle, and satisfactorily checked by an actual estimation of the heat of solution. J. C. P.

Vapour Tension of Solutions. Arrhenius' Hypothesis. By A. PONSOT (*Compt. rend.*, 1901, 133, 341—344).—From a consideration of the equilibrium of the system $\text{Zn} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2 + \text{ZnSO}_4$, the author deduces the following generalisation: "If, in a solvent which takes no part in the chemical reaction, the substitution of *A* for *B* in the compound *BC* develops heat, then the vapour tension is higher when the solvent contains any quantity of *AC* than when it contains the equivalent quantity of *BC*." Hence it must also follow that the molecular depression of the freezing point is less for the compound *AC* than for *BC*. This conclusion, although not in accord with Arrhenius' hypothesis, in which the cryoscopic modulus, &c., is independent of the nature of the radicle, is not contradicted by the experimental observations of cryoscopic depressions, or of the vapour pressure of saline solutions. L. M. J.

Thermal Study of the Solid Hydrates of Potassium Hydroxide. By ROBERT DE FORCRAND (*Compt. rend.*, 1901, 133, 157—159).—The heats of dissolution of samples of potassium hydroxide containing various quantities of combined water show that besides the compounds KOH and $\text{KOH}, 2\text{H}_2\text{O}$ there exist two intermediate hydrates, $\text{KOH}, \frac{1}{2}\text{H}_2\text{O}$ and $\text{KOH}, \text{H}_2\text{O}$. The heat of fixation of the first half-mol. of water to KOH sol. is +6.30 Cal., and that of the second half-mol. +3.15 Cal., the heat developed on passing from $\text{KOH}, \text{H}_2\text{O}$ to $\text{KOH}, 2\text{H}_2\text{O}$ being +3.04 Cal. The values for the addition of a whole mol. of water in the three cases are 12.60, 6.30, and 3.04 respectively: numbers which stand in the simple ratio, 4:2:1.

W. A. D.

Thermal Properties of Solid Hydrates of Sodium Hydroxide. By ROBERT DE FORCRAND (*Compt. rend.*, 1901, 133, 223—226).—The following heats of dissolution were obtained, NaOH + 10.305 Cal.; $\text{NaOH} + 0.32\text{H}_2\text{O}$, +9.15 Cal.; $\text{NaOH} + 0.525\text{H}_2\text{O}$, +8.08 Cal.; $\text{NaOH} + 0.644\text{H}_2\text{O}$, +7.22 Cal.; $\text{NaOH} + 0.821\text{H}_2\text{O}$, +6.18 Cal., and $\text{NaOH} + \text{H}_2\text{O}$, +5.20 Cal. The results indicate the existence of a hydrate $3\text{NaOH}, 2\text{H}_2\text{O}$ in addition to the hydrate $\text{NaOH}, \text{H}_2\text{O}$, but there is no evidence of the formation of any intermediate hydrates.

As in the case of potassium hydroxide, combination with the first quantities of water develops less heat than combination with subsequent quantities. Anhydrous potassium hydroxide is more hygroscopic than anhydrous sodium hydroxide, but after some water has been taken up, the sodium hydroxide becomes the more hygroscopic of the two. The curves of the heats of dissolution cross at a point corresponding with $\text{KOH}, \frac{1}{3}\text{H}_2\text{O}$ and $\text{NaOH}, \frac{1}{3}\text{H}_2\text{O}$, but beyond this point the heat of dissolution of the sodium compound is higher than that of the corresponding potassium compound.

C. H. B.

The Boiling Point Curve of Mixtures of Ethyl Alcohol and Water. By WILLIAM A. NOYES and R. R. WARFEL (*J. Amer. Chem. Soc.*, 1901, 23, 463—468).—The boiling points of mixtures of alcohol and water in proportions varying by 0.5 per cent. of alcohol have been determined. The mixture of lowest boiling point (78.174°) is that which contains 96 per cent. by weight (97.45 per cent. by volume) of alcohol. A mixture containing 90.7 per cent. (by weight) of alcohol has the same boiling point (78.300°) as absolute alcohol. J. McC.

Solubility of Mixtures of Copper Sulphate and Sodium Sulphate. By GUSTAVE MASSOL and MALDÈS (*Compt. rend.*, 1901, 133, 287—289).—It has been shown by Rudorff that at 15° the composition of a solution of copper sulphate (A) and sodium sulphate (B) remains invariable if both salts are in excess. The author has extended the research to temperatures of 10° , 30° , and 50° , and has found the compositions of the solutions when the salts are mixed respectively in the molecular proportions of (I) 3:1, (II) 1:1, (III) 1:3. The results obtained are given in the following table:

| | 10° . | | 15° . | | 30° . | | 50° . | |
|----------|--------------|-------|--------------|-------|--------------|-------|--------------|-------|
| | A. | B. | A. | B. | A. | B. | A. | B. |
| I..... | 19.75 | 12.49 | 20.69 | 15.88 | 22.03 | 16.36 | 32.37 | 11.75 |
| II..... | 19.70 | 12.50 | 20.75 | 15.90 | 21.00 | 20.14 | 31.45 | 13.41 |
| III..... | 19.69 | 12.55 | 20.70 | 15.92 | 15.28 | 22.70 | 28.76 | 15.25 |

It is seen that at higher temperatures the composition of the solution varies with the relative quantities of the salts, although both are present in excess.

L. M. J.

Molecular Weights at the Boiling Point. By ROBERT DE FORCRAND (*Compt. rend.*, 1901, 133, 368—371).—The law that the heat of solidification of the molecule of a gas is proportional to the absolute temperature of its boiling point at normal pressure (this vol., ii, 372) may be expressed by the equation $(L + S)/T = K = (30)$, where S is the latent heat of fusion and L the latent heat of vaporisation. This law, which has been verified for a number of substances, may be employed to find the molecular weight, and hence the molecular complexity of compounds at the boiling point. The following values for the latter constant are thus obtained. Bromine, 2.07; acetic acid, 1.61; iodine, 3; mercury, 1.18; sulphur, 8.31; nitric acid, 1.37; nitrogen pent-

oxide, 0.74. These results are in accord with those obtained by other methods, the values for iodine and sulphur agreeing with those of Oddo and Serra (Abstr., 1900, ii, 73). L. M. J.

Maxwell's Law $K=n^2$ in Reference to the Molecular Structure of Substances. By A. BATSCINSKI (*Zeit. physikal. Chem.*, 1901, 38, 119—121).—The expression $\mu = (K-1)/(K+2)$ in Mossotti's theory of dielectrics is based on two assumptions; (1) that the particles of the substance are spherical, (2) that they do not touch. The formula fails in those cases where $K > n^2$. The author, in this preliminary paper, shows that if a number of particles touch each other and lie on the surface of a sphere, K is greater than n^2 ; the difference $K-n^2$ is greater or smaller according as the sphere is hollow or filled completely with the particles of the substance. Such an aggregation of particles is supposed to exist in liquids which are undoubtedly associated; these liquids, for example, water, the alcohols, and the organic acids, generally have a large value for K . In liquids that are non-associating, and yet have a large value of K , there may be an arrangement of the atoms similar to that of the molecules described above. J. C. P.

Chemical Processes in the System: Ether—Water—Hydrogen Chloride. By FERENCZ JUTTNER (*Zeit. physikal. Chem.*, 1901, 38, 56—75).—As was observed by Schuncke (Abstr., 1894, ii, 378), ether is more soluble in an aqueous solution of hydrogen chloride than in pure water, and its solubility rapidly increases as the concentration of the hydrogen chloride rises. Since the addition of an electrolyte to a solvent generally has the opposite effect on its dissolving power (compare Rothmund, Abstr., 1900, ii, 467), it may be supposed that ether forms a compound with hydrogen chloride. All excess of ether can be expelled from its solution in hydrochloric acid by distillation or by shaking with much water, but this does not disprove the existence of a compound; these processes simply upset the equilibrium (compare the effect of distilling an aqueous solution of ferric chloride). Analogy makes it probable that a compound of ether and hydrogen chloride does exist, for the compounds $\text{Et}_2\text{O} \cdot \text{HI}$ and $\text{Me}_2\text{O} \cdot \text{HCl}$ are known. The author shows that the phenomena of the partition of hydrogen chloride between water and ether can be explained only by the existence of such a compound, and proves that this compound must be much more soluble in water than in ether, hence the increased solubility of ether in hydrochloric acid. The application of the law of mass action and van't Hoff's formula, $2\log_e(K_2/K_1) = q\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$, makes it probable that the formula is $[\text{Et}_2\text{O} \cdot \text{HCl}]_2$, although this cannot be definitely proved. In this compound, ether acts like a basic substance, and its ability to do so is attributed to the presence of quadrivalent oxygen; the case is parallel to that of dimethylpyrone hydrochloride (Collie and Tickle, *Trans.*, 1899, 75, 710), and tetramethylpyrone hydrochloride (Collie and Steele, *Trans.*, 1900, 77, 961). J. C. P.

The Colour of Ions. By G. VAILLANT (*Compt. rend.* 1901, 133, 366—368).—Colorimetric observations with a Gouy spectro-

photometer have shown that in solutions of the permanganates of potassium, zinc, and barium, the colour is solely dependent on the concentration of the MnO_4' ion. L. M. J.

Paralysis of Platinum Catalysis by "Poisons." By GEORG BREDIG (*Zeit. physikal. Chem.*, 1901, 38, 122—124).—The author argues that Raudnitz's experiment (this vol., ii, 496) on the 'poisonous' action of hydrocyanic acid does not justify the conclusion that the catalyser is not affected by 'poisons.' J. C. P.

Model of the Nitrogen Atom demonstrating the Stereoisomerism of the Oximes By EDGAR WEDEKIND (*Annalen*, 1901, 318, 117—120).—The quinquivalent nitrogen atom is represented as occupying the centre of gravity of a pyramid with a square base. Three out of the four valencies represented by lines passing through to the basal angles of the pyramid are utilised in compounds of tervalent nitrogen. Two of these valencies being satisfied by the aldehydic or ketonic carbon atom of the oxime, one or other of the two remaining basal angles may be selected to carry the hydroxyl group, thus giving rise to *syn*- and *anti*-isomerides. G. T. M.

Improved Electric Furnace for Laboratory Use. By SAMUEL AUCHMUTY TUCKER and HERBERT R. MOODY (*J. Amer. Chem. Soc.*, 1901, 23, 473—476).—The furnace described is of the Moissan type. For details, reference must be made to the original paper. K. J. P. O.

Some Modified Forms of Physico-chemical Measuring Apparatus. By ALLERTON S. CUSHMAN (*J. Amer. Chem. Soc.*, 1901, 23, 482—485).—In order to fix the electrodes more securely in the Kohlrausch-Ostwald conductivity cell, the glass supports are fixed in the ebonite cover by means of brass set-screws with ebonite tips. This arrangement is more perfect than the ordinary one in which the supports are merely fixed by friction.

An improvement of the Ostwald burette calibrator is described, in which the pipette is provided with an etched scale. The pipette is filled to the lowest mark and the burette emptied into it from the zero mark down to 2 c.c.; the volume of this is noticed on the scale of the pipette and may be taken as the standard. The pipette is emptied to the lowest mark, and water again admitted from the burette until the meniscus stands at the 4 c.c. mark. A series of readings is made in this way, and a similar series starting at the 1 c.c. mark on the burette, and the corrections are introduced in the ordinary way. By this process, the exact standardisation of the pipette by the method of weighing is avoided. J. McC.

Inorganic Chemistry.

Physical Properties of Liquid and Solid Hydrogen. Separation of Free Hydrogen and other Gases from Air. Experiments on the Liquefaction of Helium at the Melting Point of Hydrogen. Pyroelectricity, Phosphorescence, &c. By JAMES DEWAR (*Proc. Roy. Soc.*, 1901, 68, 360—366).—A helium thermometer has given 20.5° absolute as the boiling point, and 16° absolute as the melting point, of hydrogen (compare *Trans.*, 1898, 73, 534; *Abstr.*, 1899, ii, 741; this vol., ii, 308). The lowest temperature recorded in gas thermometry is 14.5° absolute, but with solid hydrogen, with more complete isolation and lower pressure of exhaustion, it will be possible to reach 13° .

The latent heat of liquid hydrogen at its boiling point, as deduced from the vapour pressures and helium-thermometer temperatures, is about 200 units, and the latent heat of solid hydrogen is not greater than 16 units.

From (1) the percentage of liquid hydrogen which has to be quickly evaporated in order to reduce the temperature to the freezing point, and (2) the latent heat of evaporation, the average specific heat of liquid hydrogen between freezing and boiling points has been found to be about 6. It thus appears that hydrogen obeys Dulong and Petit's law, and has a greater specific heat than any other known substance.

The surface tension of hydrogen at its boiling point is about one-fifth that of liquid air under similar conditions, and about $1/35$ that of water at the ordinary temperature.

Experiment gives 1.12 as the refractive index of liquid hydrogen, whilst the calculated value is 1.11. Thus the refractivity of hydrogen, like that of liquid oxygen and nitrogen, is in accordance with theory.

Hydrogen, helium, and neon have been separated from air by two methods. By one of these, a crude, uncondensed residue was obtained amounting to $1/34000$ of the volume of air liquefied; this residue contained 32.5 per cent. of hydrogen, 8 per cent. of nitrogen, and 60 per cent. of helium, neon, &c. After removal of the hydrogen and nitrogen, the neon can be solidified by cooling in liquid hydrogen. When a current of air is passed through a spiral filled with glass wool and immersed in a liquid air-bath, the condensed gas consists mostly of xenon: if the bath is kept at a slightly lower temperature by exhaustion, and the pressure of the air current suitably reduced to prevent liquefaction, krypton is deposited along with the xenon.

Comparative experiments made with hydrogen and helium in a Cailletet apparatus seem to indicate that the critical temperature of helium is under 9° absolute. It is certain that helium has been cooled to that temperature without any appearance of liquefaction. But the author points out that the refractive index of liquid helium at about its boiling point will be about 1.03, and that, therefore, small drops of liquid helium forming in the gas near its critical point will not easily be

seen. In order to liquefy helium, the process which was successful in the case of hydrogen will have to be applied, only liquid hydrogen under exhaustion will have to be used as the primary cooling agent instead of liquid air. Experience of the cooling effect produced by the regenerating process shows that the use even of liquid helium, with a probable boiling point of 5° absolute, would not enable us to reach the absolute zero. To reach the temperature of 1° , another gas would have to be found as much more volatile than helium as the latter is than hydrogen.

The phosphorescence effects observed when organic substances are cooled by the use of liquid air are much more marked when liquid hydrogen is employed. When zinc sulphide is cooled to 21° absolute and exposed to light, it shows brilliant phosphorescence on the temperature rising. The intensity of photographic action is halved by lowering the temperature from that of liquid air to that of liquid hydrogen. Remarkable electrical and luminous effects are developed by placing certain crystals (especially of some platinocyanides and of uranium nitrate) in liquid hydrogen. J. C. P.

Separation of the least Volatile Gases of Atmospheric Air, and their Spectra. By G. D. LIVEING and JAMES DEWAR (*Proc. Roy. Soc.*, 1901, 68, 389—398. Compare this vol., ii, 213).—When the less volatile portions of liquid air are allowed to evaporate gradually at a slowly rising temperature, and the gas given off is spectroscopically examined from time to time, the spectra of argon, krypton, and xenon are observed in the order given. Full details are given in the paper of the apparatus used in the distillation and separation of xenon and krypton, and the wave-lengths of their rays are tabulated in full. Most prominent in the xenon spectrum are four orange rays, a group of very bright green rays, and several very bright blue rays. The krypton lines given coincide closely with those in Runge's list, but are more numerous than the latter. J. C. P.

Occurrence of Nitrogen and Helium in Uranium Minerals. By VOLKMAR KOHLSCHÜTTER (*Annalen*, 1901, 317, 158—189. Compare Tilden, *Abstr.*, 1898, ii, 383; Gautier, this vol., ii, 171, 398).—This communication contains a summary of the work of earlier investigators and an account of experiments made with the view of determining the state in which nitrogen and helium exist in minerals.

In preparing finely divided uranium, it was found that its two lower oxides behave very differently towards reducing agents; the dioxide, UO_2 , is not reduced when heated with magnesium or aluminium powder, whilst the green oxide, U_3O_8 , reacts very violently with these reagents, the reduction being conveniently moderated by the addition of a certain amount of the lower oxide. When aluminium is employed, it is advisable to use a priming of magnesium or of barium or sodium peroxide.

The *nitride*, U_3N_4 , produced when this reduction is conducted in an atmosphere of nitrogen, is exceptionally stable at high temperatures and is not attacked by solutions of the alkali hydroxides or by concentrated sulphuric or hydrochloric acid; fusion with potash results in the elimination of the nitrogen in the form of ammonia. The gaseous

constituent is evolved in the free state on heating the nitride with oxidising agents, this result being also produced in the presence of steam, ferric oxide, copper oxide, and the oxide U_3O_8 . The compound remains unchanged when heated in a current of nitrogen, but in contact with hydrogen at high temperatures a small amount of ammonia is produced; when burnt in oxygen, the nitride leaves a residue of pure U_3O_8 . This nitride is black, whereas the product obtained by heating uranium in an atmosphere of nitrogen at 1000° is stated by Moissan to be yellow.

The yield of yellow thorium *nitride*, Th_3N_4 , obtained by substituting thorium dioxide for the uranium compound in the preceding reduction is comparatively small; under these conditions of experiment, a considerable amount of dioxide remains unreduced, and since it passes into solution on treating the fused mass with water, it probably exists in the product in the form of a magnesium thorate. This nitride differs markedly from the isomeride prepared by Matignon (this vol., ii, 60 and 106); it is not decomposed by water or dilute acids, and when heated to dull redness in air or oxygen it burns with a luminous flame.

The name *metanitride* is suggested for the new compounds obtained from the metals while in the nascent state; these products are probably identical with the corresponding nitrides existing in the uranium minerals. Nitrogen is evolved on heating these minerals because of the oxidising action of the oxides (Fe_2O_3 , U_3O_8 , &c.), which are always present.

Certain experimental results seem to indicate that helium exists in these minerals in a similar state of combination, its compounds, like the above nitrides, being decomposed by the action of the oxides at high temperatures. For example, the helium in samarskite is completely eliminated when the mineral is heated in carbon dioxide, but only a portion of the gas is evolved when the experiment is conducted in an atmosphere of hydrogen. This difference is readily explained on the assumption that the oxidising agents are reduced by the hydrogen before they can react with the helium compounds.

On the other hand, it was not found possible to synthesise a helium compound by heating the gas in contact with uranium oxide or previously ignited samarskite mixed with aluminium powder, although nitrides are readily produced under these conditions in an atmosphere of nitrogen.

G. T. M.

Compounds of Telluric Acid with Iodates, Phosphates, and Arsenates. By RUDOLPH F. WEINLAND and HUGO PRAUSE (*Zeit. anorg. Chem.*, 1901, 28, 45—70. Compare Abstr., 1900, ii, 399).—A short review is given of the compounds which iodates, phosphates, and arsenates form with acids containing an element of the sixth group (S, Cr, Mo, W).

In addition to the telluriates previously described, an ammonium tellurimoniodate, $(NH_4)_2O, I_2O_5, 2TeO_3, 6H_2O$, analogous to the potassium and rubidium salts, has been produced by crystallising at the ordinary temperature. It is only at lower temperatures that the salt with $8H_2O$ is formed.

The telluriphosphates are likewise obtained by crystallisation from concentrated solutions of the components. Of these, the following are described: potassium telluridiphosphate, $1.5\text{K}_2\text{O}, \text{P}_2\text{O}_5, \text{TeO}_3, 17.5\text{H}_2\text{O}$, crystallises from the solution below 40° ; in a vacuum, it loses nearly $3/4$ of its water and becomes $1.5\text{K}_2\text{O}, \text{P}_2\text{O}_5, \text{TeO}_3, 4.5\text{H}_2\text{O}$. The rubidium salt is analogous to the second potassium compound. Sodium tellurimonophosphate, $2\text{Na}_2\text{O}, \text{P}_2\text{O}_5, 2\text{TeO}_3, 9\text{H}_2\text{O}$, is best obtained from a solution containing phosphoric acid, telluric acid, and sodium hydroxide in the proportion 2:1:2. Ammonium tellurimonophosphate, $2(\text{NH}_4)_2\text{O}, \text{P}_2\text{O}_5, \text{TeO}_3, 4\text{H}_2\text{O}$, and ammonium telluritriphosphate, $4(\text{NH}_4)_2\text{O}, 3\text{P}_2\text{O}_5, 2\text{TeO}_3, 11\text{H}_2\text{O}$, are obtained from solutions containing the components in the proportions indicated by the formulæ.

Sodium tellurimonoarsenate, $2\text{Na}_2\text{O}, \text{As}_2\text{O}_5, 2\text{TeO}_3, 9\text{H}_2\text{O}$, ammonium telluridiarsenate, $2(\text{NH}_4)_2\text{O}, \text{As}_2\text{O}_5, \text{TeO}_3, 4\text{H}_2\text{O}$, and ammonium telluritriarsenate, $4(\text{NH}_4)_2\text{O}, 3\text{As}_2\text{O}_5, 2\text{TeO}_3, 11\text{H}_2\text{O}$, corresponding with the phosphates, have been prepared, but no potassium or rubidium salts could be obtained.

The crystallographic relationships of all the compounds have been measured.

The authors discuss the constitution of the various compounds in the light of Blomstrand's theory of the constitution of the molybdoiodates (Abstr., 1890, 107). J. McC.

Decomposition of Sodium Nitrate by Sulphuric Acid. II. By C. W. VOLNEY (*J. Amer. Chem. Soc.*, 1901, 23, 489—492. Compare Abstr., 1892, 941).—When a mixture of sulphuric acid and sodium nitrate is heated at a temperature below 100° until no more nitric acid distils over, the residue in the retort consists of unchanged sodium nitrate and an oil, which, on cooling, crystallises. The crystals have approximately the composition $\text{NaH}_3(\text{SO}_4)_2$. If the mixture is heated at a temperature of 121° until no more acid distils over, the residue consists only of sodium hydrogen sulphate. In the first period of the reaction, pure nitric acid is obtained; in the second period, a somewhat diluted acid is produced. K. J. P. O.

Cæsium Compounds. By CAMILLE CHABRIÉ (*Compt. rend.*, 1901, 133, 295—297. Compare this vol., ii, 314).—In order to completely decompose pollux, it is advisable to dry the very finely divided mineral at 130° , and then add it to about 100 times its weight of pure hydrofluoric acid. The following salts are described. *Cæsium hydrogen sulphite*, CsHSO_3 , obtained as a white precipitate on saturating an alcoholic solution of the carbonate with sulphur dioxide; *cæsium sulphite*, Cs_2SO_3 , snow-white crystals; *cæsium thiosulphate*, $\text{Cs}_2\text{S}_2\text{O}_3$, colourless needles; *cæsium dithionate*, $\text{Cs}_2\text{S}_2\text{O}_6$, obtained from cæsium sulphate and barium dithionate, large hexagonal plates. All these compounds are readily soluble in water. J. J. S.

[Non-existence of Ammonium at -95°]. By OTTO RUFF (*Chem. Centr.*, 1901, ii, 391; from *Ber. Deut. pharm. Ges.*, 11, 277—288).—A saturated solution of ammonium iodide in liquid ammonia, cooled to -95° by means of liquid air, was subjected to electrolysis. At the positive pole, nitrogen iodide separated, but at the negative pole only

hydrogen was evolved, being obviously derived from the decomposition of ammonium into ammonia and hydrogen. E. W. W.

Reaction between Chlorine and Ammonia. By WILLIAM A. NOYES and ALBERT C. LYON (*J. Amer. Chem. Soc.*, 1901, 23, 460—463).—It is shown that the normal reaction between ammonia and chlorine is represented by the equation: $12\text{NH}_3 + 6\text{Cl}_2 = \text{N}_2 + \text{NCl}_3 + 9\text{NH}_4\text{Cl}$, the volume of nitrogen being one-sixth that of the chlorine. If the ammonia is present in excess, it reacts with the nitrogen chloride, giving free nitrogen and probably also ammonium hypochlorite, thus: $\text{NCl}_3 + \text{NH}_3 = \text{N}_2 + 3\text{NH}_4\text{Cl}$ and $\text{NCl}_3 + \text{NH}_4\text{OH} + \text{H}_2\text{O} = 3\text{NH}_4\text{ClO}$. If the chlorine is present in excess, the ammonium chloride which is formed reacts with it to some extent, and little or no nitrogen is evolved.

The nitrogen chloride was estimated by extracting the product of the reaction with benzene. The benzene solution was shaken with excess of arsenious oxide dissolved in a solution of sodium hydrogen carbonate, and the excess of the oxide determined by standard iodine. After titration, the ammonia was estimated by distillation. K. J. P. O.

Action of Silver on Hydrogen Bromide and the Inverse Reaction. By JOUNIAUX (*Compt. rend.*, 1901, 133, 228—231).—When silver is heated with hydrogen bromide in sealed tubes, the action is at first rapid, but after a time equilibrium is reached, and is maintained at any given temperature, even if the heating is much prolonged. The action of hydrogen on silver bromide is analogous, and the limiting pressures at a given temperature are identical in the two cases. If hydrogen is introduced at different pressures into the tube containing the silver bromide, the proportion of hydrogen bromide formed when equilibrium is attained at a given temperature, is higher the lower the initial pressure. The results are in accord with the law of the displacement of equilibrium by variations of temperature, and the observed and calculated results agree closely. C. H. B.

Action of Cupric Hydroxide on Solutions of Metallic Salts. By A. MAILHE (*Compt. rend.*, 1901, 133, 226—228).—The cupric hydroxide, $\text{Cu}_2\text{O}_3(\text{OH})_2$, acts on solutions of several metallic bromides and chlorides at the ordinary temperature, yielding crystalline basic double bromides or chlorides. In this way, the following compounds were obtained: $\text{ZnCl}_2, 3\text{CuO}, 4\text{H}_2\text{O}$, small, blue plates or hexagons; $\text{ZnBr}_2, 3\text{CuO}, 4\text{H}_2\text{O}$, green, stellate crystals; $\text{MnCl}_2, 2\text{CuO}, 6\text{H}_2\text{O}$, a green powder consisting of minute hexagons; $\text{CoCl}_2, 3\text{CuO}, 4\text{H}_2\text{O}$, a green, crystalline powder (hexagons); $\text{NiCl}_2, 2\text{CuO}, 6\text{H}_2\text{O}$, a pale green, crystalline powder; $\text{NiBr}_2, 2\text{CuO}, 2\text{H}_2\text{O}$, in green, quadrangular lamellæ, and $\text{CdCl}_2, 2\text{CuO}, 6\text{H}_2\text{O}$, a grey, crystalline powder. The black oxide and the blue hydroxide as a rule yield the same products, but if the liquid is heated, the basic compounds may contain less water of crystallisation. The blue hydroxide, with nickel chloride in the cold, yields the compound $\text{NiCl}_2, 3\text{CuO}, 4\text{H}_2\text{O}$.

Mercuric chloride and bromide are not affected by cupric oxide or hydroxide in the cold, but if boiled with the blue hydroxide, mercuric chloride yields a green, amorphous compound, $\text{HgCl}_2, 3\text{CuO}, \text{H}_2\text{O}$.

C. H. B.

Preparation of pure Cerium Oxide. By JEAN STERBA (*Compt. rend.*, 1901, 133, 221—223).—The method of Wyruboff and Verneuil (Abstr., 1897, ii, 452) can be made more rapid by oxidising the cerous nitrate to ceric nitrate by means of a current of about 0·7 ampere and 2 volts, the liquid containing about 1 per cent. of nitric acid. The ceric oxide is precipitated with ammonia and a small quantity of ammonium sulphate, and the precipitate washed with water containing 5 per cent. of ammonium nitrate and 1 per cent. of ammonium sulphate. The process is repeated until the substance shows no absorption spectrum. Cerium oxide, free from other metals, will show a reddish coloration if it contains small quantities of nitrogen. It is slightly reduced by hydrogen at a high temperature, and is also reduced when heated with zinc, but not when heated with cadmium.

C. H. B.

Crystallised Cerium Oxide. By JEAN STERBA (*Compt. rend.*, 1901, 133, 294—295).—When fused with sodium chloride, borax, or potassium sulphate, cerium oxide forms colourless, transparent cubes, or combinations of cubes and octahedra of sp. gr. varying from 7·314 to 7·995.

J. J. S.

Neodymium Chloride. By CAMILLE MATIGNON (*Compt. rend.*, 1901, 133, 289—291. Compare Abstr., 1900, ii, 142).—*Neodymium chloride*, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, crystallises in large, deliquescent, rose coloured, monoclinic forms. It has a sp. gr. 2·282 at $16\cdot5^\circ/4^\circ$, and the molecular volume 156·9. Its solubility in 100 parts of water is 246·2 parts at 13° and 511·6 at 100° . An aqueous solution saturated at 13° has the sp. gr. 1·741 at $15^\circ/4^\circ$. Its heat of solution is +7·60 Cal.

When dried in a current of dry hydrogen chloride, it yields the hydrate $\text{NdCl}_3 \cdot \text{H}_2\text{O}$, which on further heating above 160° forms the anhydrous chloride, the heat of solution of which is +34·8 Cal. The anhydrous chloride dissolves readily in absolute alcohol, and ebullioscopic and cryoscopic determinations with the solution point to the simple molecular formula NdCl_3 for the substance.

J. J. S.

Supposed Alteration of the Properties of Aluminium. By PIETRO SPICA (*Gazzetta*, 1901, 31, ii, 67—72; *Boll. Chim. Farm.*, 40, 341—345. Compare Le Bon, this vol., ii, 20).—The formation of streaks of alumina when aluminium is shaken with mercury does not take place as a rule in less than two minutes, and when the oxide is removed and the process repeated, the streaks can be obtained only once, or at most twice, more. Water is decomposed only very slowly by aluminium in presence of mercury, and after a time no further decomposition occurs. When strips of aluminium are immersed in water containing a few drops of hydrochloric acid and a very small quantity of mercuric chloride, the formation of alumina may be observed in a few minutes; the strips, when removed from the liquid, oxidise very quickly in the air and decompose water, but after repeating the treatment two or three times they lose both these properties.

E. W. W.

Alloys of Aluminium and Molybdenum. By LÉON GUILLET (*Compt. rend.*, 1901, 133, 291—293. Compare this vol., ii, 512).—The dross from the crystalline alloys previously described (*loc. cit.*),

after treatment with very dilute hydrochloric acid, has yielded further crystalline products. The definite alloys so far isolated are, Al_7Mo , Al_3Mo , Al_2Mo , AlMo , AlMo_4 , and probably AlMo_{20} . The state of division of the aluminium employed in reducing the molybdic acid exercises considerable influence on the composition of the alloys obtained.

J. J. S.

Physical and Chemical Changes in Solutions of Ferric Salts. By EDUARD SCHAER (*Arch. Pharm.*, 1901, 239, 257—283 and 340—353).—The author describes the effect of dilution and of heat on the colour of solutions of ferric chloride, sulphate, nitrate, and acetate, and compares the colours of aqueous and alcoholic solutions of the same salts at ordinary and higher temperatures. The intensity of reaction of ferric salts with ferrocyanide, thiocyanate, salicylic acid, &c., is diminished by rise of temperature, but increased generally in the presence of alcohol. As pointed out by Schönbein, sulphurous acid intensifies the colour of ferric salt solutions, and the latter thereby acquire an increased power of oxidising and decolorising indigo; these observations have been confirmed and extended by the author. The varied phenomena recorded are arranged at length in tabular form. They are to be explained by two factors: (1) A hydrolytic dissociation of the ferric salt into acid and oxide, (2) an increased reactivity of the oxygen of the ferric oxide from the iron salt.

J. C. P.

Uranyl Nitrate. By F. JANDA (*Chem. Centr.*, 1901, ii, 266; from *Oesterr. Zeit. Berg-Hütt.*, 49, 325—328, and 340—342).—Uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, is prepared on the large scale by dissolving uranium pentoxide in nitric acid of sp. gr. 1.321. The pentoxide is obtained by igniting ammonium uranate in graphite crucibles. The original paper contains an account of the various phases of the process, the composition of the crude materials, the technical application of the salt, and a *résumé* of previous work.

E. W. W.

Studies on Solutions of Stannous Salts. III. By STEWART W. YOUNG (*J. Amer. Chem. Soc.*, 1901, 23, 450—460. Compare this vol., ii, 318, 390).—*Course of the reaction between stannous chloride and oxygen.* The conductivity of solutions of stannous chloride (0.16*N*) to which varying amounts of hydrochloric acid had been added was determined at 20° after oxidation. The conductivity of such solutions increases slowly, and only after some hours reaches a constant value. This increase, which is very rapid at first, is greater for solutions more concentrated with respect to hydrochloric acid than for those less concentrated. The results obtained when free oxygen, potassium dichromate, ferric chloride, hydrogen peroxide, or sodium hypochlorite was used for the oxidation were all similar. The facts that it requires some considerable time for the equilibrium to be attained, and that the increase in the conductivity is dependent on the concentration of the hydrochloric acid, lead the author to conclude that the first stage in the oxidation of stannous chloride is the formation of stannic chloride for which hydrochloric acid is necessary, and the second stage is the hydrolysis of the stannic chloride.

Kinetics of the reaction between stannous chloride and oxygen. The author discusses the reaction from the point of view that the hydro-

chloric acid takes part in the reaction in the first stage and is a product of the secondary reaction. It is shown that in certain cases the value of dx/dT may reach a maximum in reactions such as this, and Ostwald's statement that such maxima can only occur when catalytic influences are at work is too broad. J. McC.

Metathorium. By GRÉGOIRE N. WYROUBOFF (*Zeit. anorg. Chem.*, 1901, **28**, 90—91).—Stevens (this vol., ii, 391) has taken no account of the work of Wyrouboff and Verneuil (*Bull. Soc. Chim.*, 1899, [iii], **21**, 118; also *Abstr.*, 1899, ii, 224) on the polymeric thoric oxides. It was there shown that many oxides possess the power of polymerising, and the product acts as a bivalent radicle. The compounds with acids belong to the group of "complex" compounds. Metathorium oxide [the author regards thorium as bivalent and writes this $(\text{ThO})_n$] combines with acids without elimination of water, thus with hydrochloric acid $(\text{ThO})_n 2\text{HCl}$ is formed. On several points, Stevens' work is not in agreement with the author's. J. McC.

Atomic Weight of Antimony. By G. CLAUSEN FRIEND and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1901, **23**, 502—505).—Pure potassium antimonyl tartrate was heated in a stream of hydrogen chloride and the potassium chloride thus formed freed from carbon by ignition in a current of oxygen. The residue was then extracted with water, and the solution of potassium chloride evaporated in a platinum dish. Eight determinations of the atomic weight were made, and the mean value obtained was 120.353 ($O=16$), the maximum and minimum values differing by 0.074. K. J. P. O.

Mineralogical Chemistry.

[Berzelianite from] the Skrickerum Mine [Sweden]. By E. SVEDMARK (*Zeit. Kryst. Min.*, 1901, 34, 693; from *Teknisk Tidskrift*, 1899).—The Skrickerum mine, in the parish of Tryserum, Government Kalmar, Sweden, is noted for the selenium minerals, eucairite, berzelianite and crookesite, which it has yielded, and it was from here that Berzelius in 1818 described the first mineral containing this element. The selenium minerals occur in a small calcite vein: the berzelianite as a dusty impregnation in the calcite, and the more rarely occurring eucairite as small, silver-white to blue-grey, malleable grains. Associated minerals are native silver and copper, cuprite, several iron silicates, carbonaceous pitchblende, uranium ochre, &c.

The amount of berzelianite impregnating the calcite varies from a trace to 10 per cent. of the whole mass, and on an average is about 3 per cent. An analysis by C. G. Särnström of the pure berzelianite gave:

| Se. | Cu. | Ag. | Au. | Total. |
|-------|-------|------|--------|----------|
| 39.22 | 57.21 | 3.51 | 0.0073 | 99.9473. |

L. J. S.

Natural Cadmium Oxide. By B. NEUMANN and E. WITTICH (*Chem. Zeit.*, 1901, 25, 561—562).—A specimen of calamine from Monte Ponì, Sardinia, was covered with a dark-brown, amorphous crust, which contained some small, very lustrous crystals. These consisted of cadmium oxide, belonged to the cubic system, had a hardness about 3 and a sp. gr. 6.15. No traces of cadmium were found in the calamine.
R. H. P.

Turgite from the Uspensk Mine, South Urals. By J. SAMOILOFF (*Zeit. Kryst. Min.*, 1901, 34, 701; from *Bull. Soc. Imp. Nat. Moscou*, 1899, 1, 142—165).—An earthy iron-ore from this mine gave in four analyses the following extreme values, proving it to be turgite, $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

| Fe_2O_3 . | Mn_2O_3 . | H_2O . | Sp. gr. |
|---------------------------|---------------------------|------------------------|---------|
| 90.1—91.6 | 2.8—3.9 | 4.3—6.0 | 4.63 |

The amount of water expelled at 110° varied from 1.8 to 3.2 per cent. in the four samples. The presence of manganese sesquioxide suggests the existence of a hydrate, $2\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$, corresponding with turgite. The several minerals associated with this iron-ore are each described.
L. J. S.

Transformation of Mirabilite into Thenardite. By S. SCHEMTSCHUSCHNY and NICOLAI KURNAKOFF (*Zeit. Kryst. Min.*, 1901, 34, 700; from *Verh. russ. min. Ges.*, 1899, 37; *Protoc.* 49—52).—It is a known fact that when sodium chloride is added to a solution of sodium sulphate there may be a separation of crystals of anhydrous sodium sulphate even at the ordinary temperature. It is shown that the same reaction takes place in salt lakes in nature, for example, in the Mormischan Lake in Tomsk, Siberia. Here, under certain conditions, depending on the season of the year and the temperature of the water, the relative amounts of salt and mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) may be such that crystals of thenardite (Na_2SO_4) are deposited.
L. J. S.

Celestite from Marienstein, Bavaria. By P. VON SUSTSCHINSKY (*Zeit. Kryst. Min.*, 1901, 34, 563—568).—A crystallographic description is given of the bluish celestite which, with crystals of calcite, lines drusy cavities in a greenish-grey marl mined for the manufacture of cement at Marienstein, near Tegern Lake. Three habits of crystals are distinguished [$a : b : c = 0.77918 : 1 : 1.2824$] $2E_N = 86^\circ 50'$. Analysis gave:

| SO_3 . | SrO . | BaO . | CaO . | Total. | Sp. gr. |
|-----------------|----------------|----------------|----------------|--------|---------|
| 44.73 | 52.21 | 1.16 | 1.58 | 99.68 | 3.99 |

The calcium, which was separated by the ether-alcohol method, was found by spectroscopic examination to still contain a little strontium.
L. J. S.

Solubility of Quartz in Solutions of Sodium Tetraborate. By GIORGIO SPEZIA (*Atti Accad. Sci. Torino*, 1900—1901, 36, 631—639).—On heating quartz in a closed vessel with a 5 per cent. solution of borax at a temperature of 290 — 315° , the author finds that at the end of 4 days, 0.257 gram on an original weight of 1.0678

grams of quartz was dissolved; the quartz showed deep etchings and a deposit of hydrated silica was found on the walls of the containing vessel. The solubilities of the quartz parallel and perpendicular to the axis are different. The pressure in the above experiment was 76—106 atmospheres, but at a temperature of 12—16° and a pressure of 6000 atmospheres, borax solution does not dissolve quartz. These results indicate that mineral waters containing borax at a depth in the earth's crust corresponding with the high temperature necessary for their action may be energetic solvents of quartz. It is more probable also that the borosilicates stable at the ordinary temperature, such as tourmaline, axinite and datolite, are formed at high temperatures in the wet way by the help of solutions of sodium borosilicate than by means of volatile chlorides and fluorides, as has been previously suggested.

T. H. P.

Analyses of Minerals from the Neighbourhood of Polička. By FRANTIŠEK KOVÁŘ (*Zeit. Kryst. Min.*, 1901, 34, 704; from *Rozpravy České Akad. [Memoirs Bohemian Acad.]*, 1899, 8, No. 28, 12 pp.).—I, Pleonaste from Unter-Lhota in Moravia: dark brown to black in primitive limestone. II, Kyanite from Trpín in Moravia: in limestone. III, Grammatite (tremolite) from Bistrau in Bohemia: yellowish-green with silky lustre in veins in primitive limestone. IV, Coccoilite from the same limestone: leek-green grains. V, Gibbsite from Klein-Tresny in Moravia: greyish-white nodules with internal radial to platy structure.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | CaO. | MgO. | H ₂ O. | Total. | Sp. gr. |
|------|--------------------|----------------------------------|----------------------------------|------|-------|-------|-------|-------------------|--------|---------|
| I. | 0.98 | 62.96 | 8.81 | 3.17 | — | — | 24.70 | — | 100.25 | 3.81 |
| II. | 37.23 | 62.50 | — | — | trace | 0.14 | — | 0.19 | 100.06 | 3.50 |
| III. | 57.01 | 0.29 | — | 0.95 | — | 13.62 | 27.98 | 0.33 | 100.18 | 2.96 |
| IV. | 53.92 | 0.17 | — | 7.80 | trace | 23.13 | 14.66 | 0.14 | 99.82 | 3.26 |
| V. | 1.03 | 64.92 | trace | — | — | 0.17 | trace | 34.12 | 100.24 | 2.37 |

VI. Manganocalcite as pale rose-red spherical and botryoidal aggregates in limonite filling a crevice in limestone in a graphite mine at Gross-Tresny, Moravia.

| | CaO. | MgO. | MnO. | FeO. | CO ₂ . | Insol. | Total. |
|-----|-------|------|------|------|-------------------|--------|--------|
| VI. | 42.63 | 2.48 | 8.91 | 1.64 | 42.97 | 1.86 | 100.49 |

VII. At the last-named locality is found a mixture of realgar and orpiment, which is at first plastic but hardens on exposure to air. The orpiment seems to have been derived from the realgar, which itself has probably been derived from the mispickel and pyrites which are abundantly present.

| | As. | S. | Fe. | H ₂ O. | Insol. | Total. |
|------|-------|-------|-------|-------------------|--------|--------|
| VII. | 58.50 | 32.12 | trace | 0.93 | 8.06 | 99.61 |

L. J. S.

[Analyses of Moravian Minerals.] By FRANTIŠEK KOVÁŘ (*Zeit. Kryst. Min.*, 1901, 34, 706; from *Zeit. chem. Ind. Prag*, 1899).—A compact, very soft mineral resembling pinite occurs in crevices in limestone at Unter-Lhotka, near Kunststadt, in Moravia. It has a splintery fracture, and is translucent at the edges. Analysis gave the results

under I. The mineral is similar to Laspeyres' hygrophilite, but has been derived from feldspar and not from cordierite.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | CaO. | MgO. | (K,Na) ₂ O. | H ₂ O. | Total. | Sp. gr. |
|-----|--------------------|----------------------------------|----------------------------------|------|------|------|------------------------|-------------------|--------|---------|
| I. | 48·56 | 31·72 | 0·28 | 3·17 | 0·95 | 0·33 | 6·25 | 9·28 | 100·54 | 2·65 |
| II. | 83·30 | 0·44 | 7·08 | — | — | 0·35 | trace | 9·17 | 100·34 | 2·24 |

Ferruginous opal, occurring with hornstone in mica-schist at Rovečín, near Kunststadt, gave, on analysis, the results under II. L. J. S.

Laumontite from the Caucasus. By PETR A. ZEMJATSCHENSKY (*Zeit. Kryst. Min.*, 1901, 34, 702; from *Trav. Soc. Imp. Nat. St. Pétersbourg, Compt. rend.*, 1899, Nos. 1—2, 15—20, 30—32. Compare Abstr., 1896, ii, 369).—The following analysis is given of crystals of laumontite found in porphyrite in a railway cutting in the valley of the Bambak-tschaty River, 126 kilometres from Tiflis.

| SiO ₂ . | Al ₂ O ₃ . | CaO. | H ₂ O. | Total. |
|--------------------|----------------------------------|-------|-------------------|--------|
| 52·31 | 23·04 | 12·22 | 12·43 | 100·00 |

Heulandite from the same locality is also described. L. J. S.

Analysis of Bucklandite [Epidote]. By J. A. ANTIPOFF (*Zeit. Kryst. Min.*, 1901, 34, 699; from *Verh. russ. min. Ges.*, 1899, 37, Protoc. 45—48).—Crystals from Achmatovsk, Urals, were carefully selected for analysis, and treated with acid to dissolve calcite enclosures.

| SiO ₂ . | CaO. | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MgO. | CeO ₂ . |
|--------------------|--------------------|----------------------------------|----------------------------------|--------|---------|--------------------|
| 35·32 | 28·12 | 16·90 | 12·31 | 4·06 | 0·28 | 0·81 |
| K ₂ O. | Na ₂ O. | TiO ₂ . | H ₂ O. | Total. | Sp. gr. | |
| 0·68 | 0·11 | trace | 1·60 | 100·19 | 3·44 | |

L. J. S.

[Tremolite from Pisek, Bohemia.] By A. KREJČÍ (*Zeit. Kryst. Min.*, 1901, 34, 705; from *Sitz.-ber. böhm. Ges. Wiss.*, 1899, No. XLIX).—Notes are given on various minerals from the neighbourhood of Pisek. The following analysis was made by Schelle of white columnar tremolite from the primitive limestone:

| SiO ₂ . | (Al,Fe) ₂ O ₃ . | CaO. | MgO. | Total. |
|--------------------|---------------------------------------|-------|-------|--------|
| 53·17 | 3·02 | 25·07 | 19·31 | 100·57 |

L. J. S.

Analysis of Pyrosmalite. By FERRUCCIO ZAMBONINI (*Zeit. Kryst. Min.*, 1901, 34, 554—561).—A summary is given of the literature of this mineral. The following new analysis of material from Nordmark, Sweden, gives the formula $RCl_2, 12RO, 10SiO_2, 8H_2O$.

| SiO ₂ . | FeO. | MnO. | CaO. | MgO. | Al ₂ O ₃ . | H ₂ O. | Cl. | Total. less O for Cl. |
|--------------------|-------|-------|------|------|----------------------------------|-------------------|------|--------------------------|
| 34·71 | 27·76 | 24·30 | 0·43 | 1·11 | 0·26 | 8·31 | 4·16 | 100·10 |

L. J. S.

Meteoric Iron from Alt-Bělá, Moravia. By F. SMYČKA (*Zeit. Kryst. Min.*, 1901, 34, 707; from *Jahresber. Real-gymn. Mährisch-Osttau*, 1899).—This, the first Moravian meteoric iron, is from Alt-

Physiological Chemistry.

Respiration and Temperature of the Marmot. By MARCUS SEYMOUR PEMBREY (*J. Physiol.*, 1901, 27, 66—84).—In the active marmot, the discharge of water from the lungs is smaller, and greater variations occur in the respiratory quotient than in the rabbit. During hibernation, the discharge of water is still less; the respiratory quotient sinks to 0.53, so that the animal gains in weight. During the awakening, increased muscular activity (shivering) is seen, and metabolism becomes more active especially in relation to fats and carbohydrates; the temperature rises; so does the respiratory quotient. The discharge of moisture is only slightly augmented, so that the proportion of carbon dioxide to water may be as high as 16; in the active animal this number is 3. Cheyne-Stokes respiration is frequently seen when the torpidity is not profound. W. D. H.

Passage of Carbon Monoxide from Mother to Fœtus. By MAURICE NICLOUX (*Compt. rend.*, 1901, 133, 67—69).—Observations on animals show that the amount of carbon monoxide in fœtal and maternal blood is equal when the air breathed by the mother contains small quantities of the gas. When the percentage of the gas in the air is raised so that it is fatal, the amount in the fœtal is much less than in the maternal blood. Dissociation of the carboxyhæmoglobin is believed to occur in the placenta. W. D. H.

Sugar Formation and Enzymic Action in Liver Cells. By MANFRED BIAL (*Chem. Centr.*, 1901, ii, 315; from *Arch. Anat. Physiol.*, 1901, 249—255).—The formation of sugar in the living and 'surviving' liver is attributed to its production from glycogen by the diastatic ferment of the lymph. W. D. H.

Iron in the Hen's Egg. By PAUL HOFFMANN (*Zeit. anal. Chem.*, 1901, 40, 450—459).—An average of ten estimations showed that 100 grams of egg-yolk contain 12 milligrams of iron oxide, or 1 egg without shell 1.8 milligrams. By feeding the hens on hæmogallol or ferro-hæmol, the liver contains more iron, so also do the eggs; the hæmogallol comparatively poor in iron acts best, the amount rising by a few milligrams. By feeding with copper preparations (cuprohæmol), no copper goes into the egg. W. D. H.

Nutritive Value of Flesh. By JOHANNES FRENTZEL and MAX SCHREUER (*Chem. Centr.*, 1901, ii, 316—317; from *Arch. Anat. Physiol.*, 1901, 284—298).—For five days the nitrogen and calorific value of food, urine and faeces were estimated in a dog on pure flesh diet. 74·8 per cent. of the available energy was utilised.

W. D. H.

Metabolic Studies in Man. By A. LOEWY and FRANZ MÜLLER (*Chem. Centr.*, 1901, ii, 315; from *Arch. Anat. Physiol.*, 1901, 299—322).—The metabolic processes were studied on the authors' persons during rest and work. The absorption of nitrogenous material is much better during activity. Muscular work increases in muscle the process of assimilation, and with regard to non-nitrogenous material that of katabolism also. A good deal of nitrogen leaves the body by the sweat. Somatose was not found to be well utilised; it remains for days unabsorbed in the intestine.

W. D. H.

Value of Proteid in Nutrition. By H. LICHTENFELT (*Pflüger's Archiv*, 1901, 86, 185—193).—Metabolic studies show that the proportion between the intake and output of proteid is the same whether vegetable proteid or vegetable proteid mixed with animal proteid is given in the food.

W. D. H.

Nutrition during Training. By H. LICHTENFELT (*Pflüger's Archiv*, 1901, 86, 177—184).—Study of the diet and metabolic exchanges in athletes during training (mainly derived from Atwater's American statistics) supports the doctrine advanced by Pflüger that proteid decomposition is the main source of muscular energy.

W. D. H.

Feeding on Small Amounts of Proteid. By WILHELM CASPARI (*Chem. Centr.*, 1901, ii, 314—315; from *Arch. Anat. Physiol.*, 1901, 323—337).—These experiments on metabolism were undertaken on the author's own person; he remained in nitrogenous equilibrium while the daily supply of nitrogen was 13·3 grams, but this failed when the supply was lowered to 10 grams. Lower limits had been reached by others; the limit evidently varies in different people.

W. D. H.

Metabolism in Dogs with shortened Small Intestine. By JOSEPH ERLANGER and ALBION WALTER HEWLETT (*Amer. J. Physiol.*, 1901, 6, 1—30).—Dogs with a large amount of the small intestines removed behave much like normal dogs, so long as the diet is easily absorbable and contains only a small amount of fat. Errors in diet easily set up diarrhoea, which may prove fatal. The only noteworthy change in the urine is an increase of ethereal sulphates, indicating an excess of intestinal putrefaction.

W. D. H.

Gaseous Metabolism of the Submaxillary Gland. By JOSEPH BARCROFT (*J. Physiol.*, 1901, 27, 31—47. Compare this vol., ii, 28).—During the secretion of saliva induced by stimulation of the chorda tympani nerve, the oxygen taken from the blood by the submaxillary gland is three or four times greater than that taken by the resting organ. The carbon dioxide produced is increased to an equal or even greater

extent. After the secretory activity is stopped by atropine, the oxygen used up during stimulation of the nerve is not increased, but the output of carbon dioxide is for a time.

W. D. H.

Glycogen Formation after Proteid Feeding. By FERDINAND BLUMENTHAL and J. WOHLGEMUTH (*Chem. Centr.*, 1901, ii, 315—316; from *Berlin klin. Woch.*, 38, 391—394).—In frogs, gelatin produces no liver glycogen. Egg-white, on the other hand, containing as it does a carbohydrate radicle, leads to glycogen formation. The fact that a proteid yields leucine has no influence on the question, for both gelatin and casein yield leucine.

W. D. H.

Influence of Lecithin on Nutritive Exchanges. By G. CARRIÈRE (*Compt. rend.*, 1901, 133, 314—316).—Lecithin administered to children is stated to produce a favourable effect on their growth, and on the elements of the blood. The urea in the urine increases at first, and the phosphoric acid diminishes, but after a few months both become normal.

W. D. H.

Absorption in the Intestine. By RUDOLF HÖBER (*Pflüger's Archiv*, 1901, 86, 199—214).—A series of renewed experiments is recorded which support the conclusion that certain pigments are absorbed by the epithelial cells, but that salts, most carbohydrates, and all substances for which living protoplasm is not permeable are absorbed between the cells (compare Abstr., 1899, ii, 372).

W. D. H.

The Sugars of the Blood. By RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1901, 133, 138—139).—In dogs fed on meat, the blood gave evidence of the presence of other sugars (pentoses, lævulose, maltose, &c.) than dextrose. These are stated to be readily transformable one into the other in the blood.

W. D. H.

Excretion of Oxygen Compounds of Phosphorus. By G. GAMEL (*Chem. Centr.*, 1901, ii, 315; from *Schweiz. Woch. Pharm.*, 39, 302—303).—Insoluble metaphosphates and guaiacol phosphate pass unchanged through the alimentary canal; hypophosphites pass wholly as such into the urine, phosphites partly as such and partly as phosphates. Soluble metaphosphates, pyrophosphates, and orthophosphates are partly found in the fæces and partly as alkali phosphates in the urine. The phosphorus of guaiacol phosphite appears wholly as phosphite in the urine.

W. D. H.

Formation of Allantoin from Uric Acid in the Body. By ROBERT E. SWAIN (*Amer. J. Physiol.*, 1901, 6, 38—47).—In dogs, allantoin is excreted in the urine after ingestion of uric acid. Considerable quantities of uric acid, however, are burnt up beyond the allantoin stage. The uric acid itself is only slightly increased.

W. D. H.

Acidity of some Animal Excretions. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 133, 192—199).—The acidity of the gastric juice under normal conditions is the same whatever indicator is used, and hence must be attributed to hydrochloric acid, but under

abnormal conditions it varies with the indicator. The saliva behaves as if it contained alkali salts of very weak acids. The acidity of urine varies widely with the indicator, and also at different times with the same indicator, according to the conditions under which it was collected. C. H. B.

Actions of Currents of High Frequency and High Tension on Urinary Excretion. By DENOYÉS, MARTRE, and ROUVIÈRE (*Compt. rend.*, 1901, 133, 180—182. Compare this vol., ii, 564).—The quantity of toxic material excreted in the urine is increased by the action of the current and the effect lasts some time after the treatment. W. D. H.

Acid Poisoning in Birds. By T. H. MILROY (*Proc. Physiol. Soc.*, 1901, xii—xiv).—By making an artificial anus in birds, the urine and faeces could be collected separately; 0.5 gram per kilo. of body weight of hydrochloric acid was then given, a watery urine was passed containing scattered white flakes; the uric acid sank to about a tenth of the normal, whilst there was a great increase in the ammonia. After discontinuing the acid, normal conditions were slowly re-established. The excretion of purine bases, normally small in birds, was only slightly affected. Lactic acid produced an even more marked effect of the same kind; symptoms of acid poisoning were also more evident. If the lactic acid is neutralised with ammonia, the uric acid rose above the normal; the excretion of ammonia is also high. Nucleic acid given to birds increases the uric acid. W. D. H.

Anæmia during Gestation. By ALBERT CHARRIN and A. GUILLEMONAT (*Compt. rend.*, 1901, 133, 182—185).—The anæmia of pregnancy does not affect the corpuscular elements so much as the materials in solution in the blood; among a number of points noticed are an oscillation in the alkalinity of the blood, and an increased rapidity of coagulation (*in vitro*). W. D. H.

The Affinity of Red Blood Corpuscles for Acids and Alkalis and the Resistance so produced towards Solanine. By E. HÉDON (*Compt. rend.*, 1901, 133, 309—312).—After the red corpuscles are completely freed from serum by the centrifuge, they possess the power of fixing in their substance both acids and alkalis. This, up to a certain limit, occurs without destruction of the corpuscles or liberation of their hæmoglobin. Corpuscles so treated with acid are very resistant towards solanine, a very powerful hæmolysing agent. On the other hand, alkalis favour the hæmolysis by solanine. W. D. H.

Experimental Parthenogenesis. By YVES DELAGE (*Compt. rend.*, 1901, 133, 346—349).—Experiments on the maturation of echinoderm eggs, showing how partial development may be induced experimentally without fecundation. Special stress is laid on the maturation of the cytoplasm, rather than of the nucleus. W. D. H.

Impermeability of Skin and External Mucous Membranes to Hydrogen Sulphide By AUGUSTE CHAUVEAU and TISSOT (*Compt. rend.*, 1901, 133, 137—138).—Animals live quite well in a lethal

atmosphere containing hydrogen sulphide, provided that they are allowed to inhale pure air through a tube. W. D. H.

Physiology of the Suprarenal Capsules. By HANS STREHL and OTTO WEISS (*Pflüger's Archiv*, 1901, 86, 107—121).—Complete extirpation of both suprarenal capsules in large numbers of animals (mammals and frogs) is invariably fatal in from 8 to 138 hours. If one only is excised, the other hypertrophies; on removal of the second, death ensues. The most prominent symptom before death is muscular weakness. The blood of the suprarenal vein contains the substance which elevates blood pressure. If one capsule is extirpated, and the remaining suprarenal vein is compressed, the arterial pressure falls, and on releasing the vein the pressure rises to a height greater than the normal. Nothing new is added to the chemistry of the active substance; no spermine was found. No other organ yields a substance which raises blood-pressure. W. D. H.

Action of Pituitary Extract on the Kidney. By R. MAGNUS and EDWARD ALBERT SCHÄFER (*Proc. Physiol. Soc.*, 1901, ix—x).—Although the main effect of pituitary extract is to cause contraction of organs, it produces expansion of the kidney and diuresis, so differing from suprarenal extracts. The material which is active in this direction is soluble in water, but not in alcohol; it is derived from the nervous or infundibular portion of the pituitary body. W. D. H.

Pharmacology of Pyraconitine and Methylbenzaconine considered in relation to their Chemical Constitution. By J. THEODORE CASH AND WYNDHAM R. DUNSTAN (*Proc. Roy. Soc.*, 1901, 68, 384—389. Compare Abstr., 1899, ii, 42—43).—A detailed account is given of the physiological action of these two alkaloids. It is found that in the case of pyraconitine (*Trans.*, 1894, 65, 176), as in that of benzaconine, the great toxicity of aconitine is almost entirely abolished by the withdrawal of the acetyl group. Of the two alkaloids, benzaconine and pyraconitine, the latter is the more active, and although there is a similarity in the physiological effects which they produce, the differences are more considerable than they would be if pyraconitine were merely the anhydride of benzaconine.

The substitution in aconitine of methyl for acetyl which occurs in the formation of methylbenzaconine (*Proc.*, 1896, 12, 159) has led to a very considerable reduction of toxicity, and has introduced a curare-like effect. Methylbenzaconine is more powerful than benzaconine owing to the presence of the methyl group.

The chief action of pyraconitine on the heart is to cause slowing, partly from vagus irritation, partly from depression in function of intrinsic rhythmical and motor mechanisms. Activity of respiration is reduced (by central depression) to a degree incompatible with life, as is the case after aconitine and benzaconine. The spinal cord is impaired in its reflex function, apparently secondarily to reduced circulation in its structure. Neither muscular nor intramuscular nervous tissue is strongly influenced by large doses of the alkaloid.

The effects of pyraconitine are contrasted with those of benzaconine. The former alkaloid is about six times more toxic than the latter.

Methylbenzaconine in large doses causes slowing of the heart; the cardiac vagus is depressed in action, and its inhibitory function is ultimately suspended. Motor nerves are greatly affected, the action being curare-like in character.

The effects of methylbenzaconine are contrasted with those of aconitine and benzaconine. The toxicity of aconitine is 80 to 100 times that of methylbenzaconine, whilst the latter is about three times more toxic than benzaconine. E. G.

Pharmacology of Pseudaconitine and Japaconitine considered in relation to that of Aconitine. By J. THEODORE CASH and WYNDHAM R. DUNSTAN (*Proc. Roy. Soc.*, 1901, 68, 378—384. Compare Abstr., 1899, ii, 42—43).—The differences observed in the action of these three alkaloids are nearly always differences of degree and not of kind. They all have a similar effect upon the heart. Vagus stimulation causes slowing of the heart in each case. Pseudaconitine produces less tendency to acceleration of respiration than the other two alkaloids, whilst the dyspnoeal conditions develop more suddenly and the central depression of respiration is greater. Japaconitine is at first slightly more depressant than aconitine, but thereafter the tendency to acceleration of respiration is sooner developed. All the aconitines produce a deleterious effect on the hæmoglobin and coloured blood corpuscles. The effect on the brain and cord is the same in each case. The initial elevation of temperature produced by aconitine or japaconitine is less frequently observed with pseudaconitine, whilst a slightly greater and more enduring fall of internal temperature is witnessed after a large dose of the latter. Some tolerance is established on the part of rabbits towards all the aconitines, but less towards pseudaconitine than towards the other two. The effect of local application upon the sensory nerves is somewhat more powerfully depressant and enduring with aconitine or japaconitine than with pseudaconitine, but the difference is only slight. It is more difficult to reduce reaction or to produce insensitiveness of the intramuscular motor nerves by pseudaconitine than by the other alkaloids. Direct contact of the alkaloidal solutions with muscle-nerve preparations reduces excitability; pseudaconitine produces a rather weaker effect than the other two, of which japaconitine is slightly the more energetic. The general order of toxicity towards mammals is pseudaconitine, japaconitine, and aconitine, which is the least toxic. Pseudaconitine has been found to be about twice as toxic as aconitine towards small mammals and birds, whilst the relative toxicity of japaconitine to aconitine is approximately as ten to nine. E. G.

A Method of obtaining Intracellular Juices. By SYDNEY ROWLAND (*J. Physiol.*, 1901, 27, 53—56).—An apparatus consisting mainly of a disintegrator and a powerful press for breaking up tissues and expressing their juice is described and figured. W. D. H.

[Proximate Composition of] Nervous Tissue. By N. ALBERTO BARBIERI (*Compt. rend.*, 1901, 133, 344—346).—The portion of the brain tissue of an ox soluble in ether consists principally of fats which yield cholesterol on hydrolysis, and nucleins which furnish cerebrin.

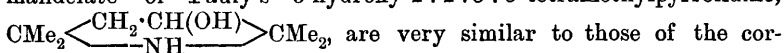
The portion soluble in water containing ether yields two globulins (α - and β -), an alkali globulin (?), a ptomaine hydrochloride, an aromatic substance, a substance intermediate between leucine and butalanine, and volatile fatty acids. The portion insoluble in both ether and water yields cerebrin, homocerebrin, keratin, and a proteose (?), along with a non-nitrogenous substance soluble in chloroform and melting at 135° , and a substance crystallising from acetone in white needles melting at 138° (erythrocholesterol?). W. A. D.

Benzoylation of Alcapton Urine. By KENNEDY J. P. ORTON and ARCHIBALD E. GARROD (*J. Physiol.*, 1901, 27, 89—94).—On the addition of benzoyl chloride and sodium hydroxide to alcapton urine, a product is formed which is at once thrown down when a hot alcoholic extract of the precipitate is poured into water. This crystallises in colourless needles which melt at 204° . It may also be prepared in a similar way from a solution of homogentisic acid in the presence of ammonia. The product in question is the amide of dibenzoylhomogentisic acid; this acid may be liberated by treatment with fuming nitric acid, and on again treating it with benzoyl chloride and sodium hydroxide in the presence of ammonia, the amide is obtained. These facts furnish an additional means of detecting homogentisic acid in the urine. W. D. H.

Combination of Glycuronic Acid with Fatty Compounds. By OTTO NEUBAUER (*Chem. Centr.*, 1901, ii, 314; from *Arch. exp. Path. Pharm.*, 46, 133—154).—The physiological action of various fatty compounds on rabbits in reference to the formation of glycuronic acid compounds has been further investigated (compare Thierfelder and Mering, *Abstr.*, 1885, 1002). The secondary fatty alcohols, and to a very much less extent the primary, with the exception of methyl alcohol and alcohols of high molecular weight, form glycuronic acid compounds. Some polyhydric alcohols, such as propylene glycol, form compounds of this type, whilst others, such as glycerol, do not. All aliphatic ketones, as well as acetophenone, partially combine with glycuronic acid, but only after being reduced to secondary alcohols, as is shown by the fact that when the glycuronic compounds are decomposed by boiling the urine with dilute sulphuric acid, the distillate does not give the ketonic reaction until it has been oxidised by potassium dichromate and sulphuric acid. Experiments with aldehydes gave doubtful results. The hydrocyclic compounds, *l*-menthone and menthene, form glycuronic acid compounds. Since normal urine contains only very small quantities of glycuronic acid compounds, and these include aromatic components, the alcohols and ketones cannot be regarded as intermediate products of processes taking place in the organism. E. W. W.

Relationships between Physiological Action, Chemical Constitution, and Chemical Change in the Organism. By HERMANN HILDEBRANDT (*Chem. Centr.*, 1901, ii, 316; from *Arch. internat. Pharmacodynamie Thér.*, 8, 499—509. Compare *Abstr.*, 1900, ii, 676).—When thymotinipiperidide is administered to rabbits, about half is excreted as a glycuronic acid compound, whilst the remainder is probably oxidised in the organism, but the proportion so oxidised is

not affected by keeping the rabbits in an atmosphere of oxygen. Piperidine itself, however, which is less poisonous than the piperidide, and is more completely oxidised in the organism, is to a certain extent rendered less poisonous by respiration of oxygen. On comparing the behaviour of diethylamine and pyrrolidine, it has been found that, unlike that of citral and *cyclocitral* (this vol., ii, 180), the chain compound is less poisonous, and probably more easily oxidised than the ring compound. The pharmacological actions of the benzoate and mandelate of Pauly's 3-hydroxy-2:2:5:5-tetramethylpyrrolidine,



are very similar to those of the corresponding piperidine derivatives, "eucaine B" and "euphthalmine," but whilst the benzoate of the pyrrolidine derivative has a similar anæsthetic action to that of "eucaine B," it is less poisonous, and the mandelate has a weaker mydriatic effect than "euphthalmine."

E. W. W.

Decomposition of Cocaine and Atropine in the Animal Organism. By WILHELM WIECHOWSKI (*Chem. Centr.*, 1901, ii, 317; from *Arch. exp. Path. Pharm.*, 46, 155—162).—After administering cocaine to dogs, 0—12 per cent. was found unchanged in the urine, whilst after similar treatment with atropine, 17—57 per cent. of the alkaloid was excreted. When cocaine is given to rabbits, however, none of the alkaloid is found in the urine. Since ecgonine and tropine, the characteristic decomposition products of cocaine and atropine, respectively, could not be detected in the urine, both alkaloids must undergo a very thorough decomposition in the organism.

E. W. W.

Chemistry of Vegetable Physiology and Agriculture.

Reaction of Bacteria to Chemical Stimuli. By HERBERT S. JENNINGS and J. H. CROSBY (*Amer. J. Physiol.*, 1901, 6, 31—37).—A new series of experiments which show that the so-called tactic phenomena exhibited by bacteria are due to a definite movement or reflex action produced by the stimulating agent. In this respect, chemical stimuli act like other irritants. W. D. H.

Oxydase in Yeast. By J. GRUSS (*Chem. Centr.*, 1901, ii, 364, 364—365, and 436; from *Woch. Brauerei*, 18, 310—312, 318—321, and 335—338. Compare Effront and Tolomei, *Atti R. Accad. Lincei*, [v], 5, 52).—As a carrier of oxygen, the oxydase of yeast resembles the oxydase obtained by the author from barley (this vol., ii, 33); it oxidises tetramethyl-*p*-phenylenediamine chloride, but not guaiacol. Pressed bottom fermentation yeast generally acts on “tetra” paper, but not when the paper is saturated with soda; with pressed top fermentation yeast, the effect is reversed. Glycerol extracts of top fermentation yeast

reduce ammoniacal silver solution, but not Fehling's solution. In the case of extracts of bottom fermentation yeast, the action on silver solutions is very slight. The reducing substance is distinguished from the oxydase by the fact that the latter cannot be extracted by glycerol. The results indicate that the effect of the oxydase on salts of tetramethylene-*p*-phenylenediamine may be masked by the reducing substance present in yeast. The reducing substance, which is produced during fermentation, is gradually destroyed by contact with air.

The oxydase is weakened by a low temperature ($0-3^{\circ}$), and by 96 per cent. alcohol, and is destroyed by heating at $60-65^{\circ}$. It is also weakened when the yeast with which it is associated is kept in pure water, whilst its power is maintained when the yeast is kept in a solution of asparagine. It is suggested that the oxydase converts asparagine into malic acid, with liberation of nitrogen and water: possibly the succinic acid found in fermenting solutions is due to the further action of the oxydase on malic acid.

Yeast oxydase seems to effect the oxidation of phenylhydrazine. Magenta and methylene-blue, decolorised by sulphur dioxide, have their colours more quickly restored in presence of yeast than without yeast.

Catalysing substances occur in nature which have no effect on guaiacol, but bring about the oxidation of di- and tetra-methyl-*p*-phenylenediamine. It is doubtful, at present, whether laccase, which acts on guaiacol, has this property. The periderm of potato tubers contains an oxydase which differs both from the spermase of barley (*loc. cit.*), and from the yeast oxydase.

It is proposed to divide the oxydases into two groups, guaiacol-oxydases and amino-oxydases.

N. H. J. M.

Buchner's Yeast Extract. By AUGUSTIN WRÓBLEWSKI (*J. pr. Chem.*, 1901, [ii], 64, 1-70).—The extract obtained by the author (this vol., ii, 465) is a somewhat viscous liquid, of aromatic odour and sweet taste, and exhibits a brownish-yellow or greyish-blue fluorescence. It is either optically inactive or feebly dextrorotatory. Filtration through a Berkefeld or sandstone filter diminishes, and through a Chamberland filter entirely removes, the fermenting power. The extract does not act on starch granules, but ferments starch paste, soluble starch, glycogen, or sucrose.

In fermentation by yeast cells, the zymase remains in the cells and does not diffuse into the sugar solution. If the cells are collected on a sandstone filter, fermentation in the sugar solution ceases. The author expresses the opinion that the sugar solution passes into the cells and is there fermented. Alcohol and carbon dioxide, accordingly, are true excreta of the yeast cells.

0.5 per cent. of neutral salts increases the fermenting action on sucrose, 1 per cent. decreases, and 2.5 per cent. completely destroys, the activity of the yeast. 0.05 per cent. of hydrochloric or acetic acid lessens the activity. Fermentation is increased by addition of 0.02 to 0.03 per cent. of sodium hydroxide, decreased by 0.1 per cent., and prevented by 0.2 per cent., when the phosphates are precipitated. Phosphates have a favourable action (compare this vol., ii, 328).

Dilution at first renders the zymase less active, and finally inactive. When the extract is diluted with a solution of phosphates, the effect is not so great. Formaldehyde inhibits fermentation when added to the amount of 0.05 per cent. 0.007 per cent. of sodium nitrite stimulates the activity of the yeast cells, but 0.035 per cent. depresses it, whilst with 0.25 per cent. nitrogen is evolved (compare Abstr., 1900, ii, 157). Nitrous acid (that is, a mixture of sodium nitrite and hydrochloric acid) has a far greater inhibiting effect than either sodium nitrite or hydrochloric acid alone. After addition of 10 per cent. of alcohol, the activity decreases, and ceases after addition of 15 per cent., whilst 20 per cent. produces a voluminous precipitate of proteids. Glycerol has little action at concentrations below 25 per cent.

The author believes that the zymase is not an enzyme, but a colloidal substance which exists in the extract in a state of semi-solution, and belongs to the group of protoplasmic ferments (compare Abstr., 1900, ii, 158).

Invertin, unlike zymase, diffuses out of the yeast cells, and cannot be filtered off (compare Abstr., 1900, ii, 158, and this vol., ii, 465). It is most active when within the cell. When prepared from yeast extract (*loc. cit.*), it is always very impure and accompanied by a carbohydrate, mannosan (compare Salkowski, this vol., i, 180), which, after warming with hydrochloric acid, reduces Fehling's solution, is precipitated by lead acetate and ammonium sulphate, does not give a reaction with iodine, and produces only a brown coloration with hydrochloric acid and phloroglucinol.

The inverting action of invertin is depressed by 0.14 per cent. of hydrochloric acid, by 0.1 per cent. of sodium hydroxide, by dilution with water, or by addition of alcohol, of large quantities of neutral salts, or of small quantities of alkaline phosphates; on the other hand, addition of acid phosphates is advantageous. Invertin is not decomposed by the proteolytic enzyme of the extract or by trypsin. In comparison with diastase, it is more readily soluble, and less easily precipitated.

In addition to substances and ferments previously found in yeast extract (Abstr., 1899, ii, 170), the presence of enzymes capable of acting on maltose, glycogen, starch, and cellulose, and of coagulating nuclealbumin, has been demonstrated. Besides the phosphates of the alkaline earths, the extract contains phosphoric acid in combination with an organic substance. This compound crystallises in small leaflets, and neither gives a peptone reaction nor reduces Fehling's solution. Glycerol, lecithin, xanthine-like substances, and formic acid are present in the extract. The ethereal extract contains fats, cholesterol, and a substance crystallising in needles. K. J. P. O.

Nitrogenous Nutrition of Yeast. By PIERRE THOMAS (*Compt. rend.*, 1901, 133, 312—314).—Ten per cent. dextrose solutions fermented slowly when supplied with nitrogen in the form of urea, and the yeast formed under these conditions is poor in nitrogen; 20 per cent. solutions fermented very rapidly and produced more highly nitrogenous yeast.

When the amount of urea is increased, the amounts of yeast formed and of nitrogen assimilated tend towards a maximum, beyond which increased amounts of urea have no effect. This seems to depend on the amount of yeast, and on the nature of the nitrogenous food (Compare Stern, Trans., 1901, 79, 943).

When ammonium hydrogen carbonate is employed instead of urea, 20 per cent. dextrose solutions are still found to give the best results. As in the case of urea, the amounts of yeast formed, and of nitrogen assimilated, are increased up to a certain point by increasing the amounts of ammonium salt; the maximum is much higher than with urea. The results, which are opposed to those obtained by Hayduck, show that the composition of yeast, as regards nitrogen, is very variable.

Yeast does not assimilate acetamide to any extent when no other nitrogenous compound is present. Assimilation took place, however, in presence of ammonium acetate.
N. H. J. M.

Production of Alcohol during the Intramolecular Respiration of Seeds in Water. By EMIL GODLEWSKI AND F. POLZENIUSZ (*Bull. Acad. Sci. Cracow*, 1901, 227—276).—A more detailed account of experiments already described (compare Abstr., 1898, ii, 400). Peas introduced into a solution of potassium nitrate appear to partially reduce the nitrate, and the products of reduction kill the seeds within the course of a few days.

It is found that free oxygen is not necessary for the formation of enzymes such as diastase and invertase in plants.

The intramolecular respiration of seeds in water free from oxygen proceeds for several weeks; it begins slowly, then attains a maximum at the end of 3 or 4 days, and after one or two weeks, or even longer, gradually diminishes. The respiration is accelerated by an increase in temperature, but does not last so long. Different varieties of seeds are capable of intramolecular respiration to varying extents. The property is most marked in the case of leguminous plants, less with cereals, and least with oleaginous, seeds. It is probable that, in all cases in which the respiration occurs at the expense of carbohydrates such as dextrose, the chemical action is practically identical with ordinary alcoholic fermentation. In other cases, where the respiration occurs at the expense of carbon compounds other than hydrolysable sugars, the action is very feeble and has not been closely investigated.

It is probable that ordinary and intramolecular respiration in plants are identical in their chemical nature when the former occurs at the expense of hydrolysable carbohydrates, but that they are quite distinct when the ordinary respiration is brought about by the oxidation of other carbon compounds.
J. J. S.

Occurrence of Sucrose in the Fruit of Paris Quadrifolia. By NICOLAI KROMER (*Arch. Pharm.*, 1901, 239, 393—395).—From the dried and powdered fruit of *Paris quadrifolia*, which had been freed from fat, alcohol extracts a sugar which proved to be sucrose.

K. J. P. O.

Composition of the Albumen of the Seeds of *Phoenix Canariensis* and the Chemical Changes accompanying their Germination. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1901, 133, 302—304).—Mannose is the chief product of hydrolysis of the crushed seed with dilute sulphuric acid. During the germination of the seed, a soluble enzyme is produced which is capable of hydrolysing the mannans of the albumen to mannose, and this sugar is utilised as rapidly as it is formed. J. J. S.

Mechanism of Esterification in Plants. By EUGÈNE CHARABOT and A. HÉBERT (*Compt. rend.*, 1901, 133, 390—391. Compare Abstr., 1898, i, 595; 1900, i, 241, 303; ii, 101, 361, 362; and this vol., i, 38).—The conclusion that etherification in plants is caused by the direct interaction of acids with alcohols, and is promoted by a special dehydrating agent, is drawn from previous results, and the following observations. (1) The esterification of linalool by acetic acid alone is much slower than that occurring in the plant; (2) the terpenic alcohols which esterify most readily with a given acid are those which are combined in the greatest proportion with this acid in plants; (3) for the same terpenic alcohol, the acid which is most readily esterified is that whose ester is most abundant in the plant; (4) when two alcohols present in a plant are esterified with the same acid, the acid is shared between them as in the plant. It is probable that the dehydrating agent is a diastase acting in a chlorophyll medium. W. A. D.

Formation of Proteids in Plants. By W. ZALESKI (*Chem. Centr.*, 1901, ii, 362; from *Ber. deut. bot. Ges.*, 19, 331—339).—The results of previous experiments with *Allium Cepa*, showing a slight increase of proteid nitrogen in relation to total nitrogen, are confirmed by experiments with onions, which show a much greater increase of proteid nitrogen. The bulbs, cut into four pieces, were placed in moist air under a bell-jar, and kept in darkness for some days. No increase of proteids takes place in an atmosphere of nitrogen.

Similar results were obtained with other roots and tubers (such as *Beta vulgaris*, *Daucus Carota*, *Petroselinum sativum*, *Apium graveolens*, *Solanum tuberosum*, and *Dahlia variabilis*) which contain considerable amounts of non-proteids and non-nitrogenous reserve substances.

N. H. J. M.

Nitrogenous Constituents of Green Leaves. By E. WINTERSTEIN (*Chem. Centr.*, 1901, ii, 360—361; from *Ber. deut. bot. Ges.*, 19, 326—330).—The leaves, extracted with boiling water, were treated successively with water rendered slightly alkaline and with 1 per cent. aqueous sodium hydroxide. The extracts precipitated with acetic acid yielded only small quantities of substance as compared with the total proteids. The residues obtained from spinach and lupins, when heated with 30 per cent. hydrochloric acid, yielded abundant precipitates with phosphotungstic acid, from which light yellow residues of the proteids were liberated by baryta. Similar results were obtained with fungi, and the author supposes that the proteids are present in combination with other groups, probably carbohydrates.

N. H. J. M.

Free Humic Acids in Mineral Soil and their Importance in Agriculture. By HEINRICH IMMENDORFF (*Bied. Centr.*, 1901, 30, 506—508; from *Mitt. Ver. Förd. Moorkult.*, 1900, 18, 13).—Four samples of sandy soil, to some of which moor soil had been applied for centuries, were found to contain 0.085 to 0.121 per cent. of free acid (reckoned as carbon dioxide), and lost on ignition 5.16 to 7.60 per cent. in the dry soil. These results indicate that the organic matter contains 1.55 to 1.84 per cent. of free acid, and closely resembles, in this respect, the humous soil originally applied. Calculating the amount of free acid per hectare to a depth of 20 cm., it is shown that the soil contains at least 2500 kilos., which would require more than 3000 kilos. of pure calcium oxide to neutralise it.

Field experiments, in which rye and potatoes were grown on peaty soil containing 0.18 per cent. of free acid, manured with Algerian phosphate, gave very satisfactory results.

The discordant results obtained by Wagner and Märcker with bone meal are perhaps due to the fact that the soils which yielded satisfactory results with bone meal contained free humic acid.

N. H. J. M.

Experiments with Different Nitrogenous Manures (Ammonia and Sodium Nitrate). By BERNHARD SCHULZE (*Bied. Centr.*, 1901, 30, 530—531; from *Jahresber. agrik.-chem. Versuchsstat. Landw.-kammer Schlesien*, 1899, 22).—Oats were grown in pots manured with 1, 2, and 3 grams of nitrogen respectively, in addition to mineral manures. The nitrogenous manures were sodium nitrate, ammonium sulphate (with and without addition of lime), and powdered bone gelatin. The effect of the three manures was almost exactly the same when 1 gram of nitrogen was applied. Larger amounts as nitrate increased the production of straw, whilst larger amounts as ammonium sulphate acted irregularly and decreased the yield of grain; bone gelatin, in quantities containing more than 1 gram of nitrogen, was injurious, owing to the rapid production of ammonium carbonate.

N. H. J. M.

Cultivated Plants and Organic Nitrogen Compounds. By ARVID THOMSON (*Bied. Centr.*, 1901, 30, 539—542; from *Sitzungsber. Naturforsch.-Ges. Univ. Jurjew (Dorpat)*, 1899, 307—322).—The results of water-culture experiments in which oats and barley were manured with urea, sodium urate, and sodium hippurate respectively, in addition to the usual minerals, showed that the growth was normal when nitrogen was present in the form of urea or uric acid. In the case of urea, the growth was nearly equal to that obtained with nitrate. Sodium hippurate proved to be unsuitable as a source of nitrogen for oats and barley.

N. H. J. M.

Manure Experiments with Crude Phosphate. By FRANZ W. DAFERT (*Chem. Centr.*, 1900, ii, 223; from *Zeit. Landw. Versuchs-Wes. Oesterr.*, 4, 627—629).—Algerian phosphate increased the yield of clover very considerably, and it is hoped that the action of the manure will extend beyond the first year.

N. H. J. M.

Influence of Potassium Salts on the Development of Barley. By JULIUS STOKLASA and J. PITRA (*Chem. Centr.*, 1901, ii, 223 ; from *Zeit. Landw. Versuchs-Wes. Oesterr.*, 4, 567—582).—The results of pot experiments showed that the application of a moderate amount of potassium chloride, in conjunction with superphosphate and sodium nitrate, was favourable both as regards the yield and the quality of the barley. The larger grain was unusually rich in starch, and contained relatively small amounts of proteids, spelt, and pentoses.

The same combination of manures was found to be very suitable for the production of brewing barley. N. H. J. M.

Free Iodine in Sodium Nitrate. By FRANZ W. DAFERT and AD. HALLA (*Chem. Centr.*, 1901, ii, 368—369 ; from *Zeit. Landw. Versuchs-Wes. Oesterr.*, 4, 732—734).—A sample of sodium nitrate was found to contain free iodine and potassium iodate (0·4 per cent.), but no iodide. The presence of free iodine is attributed to the action of organic matter (in this case, barley grains) on the iodate. N. H. J. M.

Plot and Pot Experiments with different Potassium Salts. By BERNHARD SCHULZE (*Bied. Centr.*, 1901, 30, 531—534 ; from *Jahresber. agrik.-chem. Versuchsstat. Landw.-kammer Schlesien*, 1899, 25).—Potassium chloride (40 per cent.) and kainite both increased the yield of sugar beet and the yield of sugar, whilst potassium sulphate had no effect. All three manures, when applied to potatoes diminished the yield of starch.

The results of the author's experiments indicate that potassium chloride and kainite do not differ essentially in their action as manures, but that potassium chloride is more completely utilised than kainite.

N. H. J. M.

Experiments with Excrement. By KRENZ and MAX GERLACH (*Bied. Centr.*, 1901, 30, 519—522 ; from *Jahresber. landw. Versuchsstat. Jersitz, Posen*, 1898—1899, 20).—Concentrated excrement was found to vary very considerably in composition, especially as regards nitrogen. When kept in pits, there is a great loss of nitrogen, mainly in the form of ammonia. It is therefore important that the manure should be applied to the soil as soon as possible, or else mixed with soil or peat. Human excrement is free from substances which promote the activity of denitrifying organisms.

N. H. J. M.

Analytical Chemistry.

Gas Analysis Apparatus. By A. SAMOILOFF and A. JUDIN (*Chem. Centr.*, 1901, ii, 229—231 ; from *Arch. Anat. Phys., Physiol. Abt.*, 1901, 338—352).—A modification of the apparatus described by Schaternikoff and Setschenoff (*Abstr.*, 1896, ii, 332) ; also a description of a new form of a gas pipette which cannot be well understood without the accompanying illustrations.

L. DE K.

Apparatus and Procedure for Exact Incineration. By HEINRICH WISLICENUS (*Zeit. anal. Chem.*, 1901, 40, 441—449).—For completely burning the organic part of a vegetable substance without the loss of any of the mineral constituents, the author has devised a special form of cover for an ordinary platinum basin. This permits the admission of air or oxygen during the incineration, warms the gas, and then introduces it quietly round the periphery. The cover has a tube in the centre by which it can be connected with a condenser (of Jena glass), and the latter is joined to an absorption apparatus (to be described hereafter) in which milk of lime is placed, and through which air can be aspirated by a pump. Any mineral substances volatilised during the incineration are arrested in this absorber. The preliminary carbonisation of the substance is assisted by adding a solution of calcium acetate and oxide and drying on the sand-bath before burning. After charring in the open basin, the cover and absorption apparatus are adjusted, a slow current of air established, and the incineration carried as far as is possible at a dull red heat, washed oxygen being admitted towards the close. Should any particles of carbon still remain unburnt, the ash is moistened with pure (3 per cent.) hydrogen peroxide, dried, and reheated. M. J. S.

Commercial Hydrogen Peroxide. By GEORGES ARTH (*Chem. Centr.*, 1901, ii, 445—446; from *Mon. sci.*, [iv], 15, ii, 435—436).—For the detection of oxalic acid, said to be occasionally met with in the commercial product, the following process is recommended: 100—200 c.c. of the sample are rendered faintly alkaline with ammonia, and calcium chloride is added. The precipitated calcium oxalate is washed with ammoniacal water until the acidified washings are no longer affected by permanganate; the oxalate is then titrated as usual. According to the author, the oxalate is often contaminated with hydrated calcium dioxide, and the titration, therefore, becomes uncertain.

For titrating the peroxide, a solution containing 5.659 grams of potassium permanganate per litre is recommended, as each c.c. of this corresponds with 1 c.c. of available oxygen by volume in the sample.

L. DE K.

Oxidation of Nitrogen as a Source of Error in the Estimation of Nitrogen and Methane. By ALFRED H. WHITE (*J. Amer. Chem. Soc.*, 1901, 23, 476—482).—Oxides of nitrogen soluble in aqueous potassium hydroxide are always formed in explosion analysis. With Bunsen's eudiometer, the error is only trifling, but when Hempel's pipette is used it may amount to 1 per cent. or more, particularly if methane is present. The error may, however, be reduced to a minimum by keeping the explosive ratio between four and three. The method of Dennis and Hopkins (burning the mixture of methane or hydrogen with air by means of a red hot platinum spiral) also tends to yield soluble oxides of nitrogen if the spiral is heated too strongly or too long.

L. DE K.

Estimation of Sulphur in Coal, Bitumen, Pyrites, Roasted Ores, Products of Scorification, &c. By HENRI PELLET (*Ann. Chim. anal. appl.*, 1901, 6, 281—285).—One gram of the dry and

finely powdered substance is mixed with an oxidising flux composed of 20 grams of dry sodium carbonate and 10 grams of potassium nitrate, and the whole fused in a platinum crucible, avoiding the use of coal-gas. The mass is then dissolved in water, the filtrate acidified with hydrochloric acid, and precipitated with barium chloride; the ignited barium sulphate is washed and reweighed.

To estimate volatile, so-called injurious, sulphur, another gram of the sample is roasted, and the sulphur in the residue, which exists as sulphate, is again estimated by boiling the mass with dilute hydrochloric acid and adding barium chloride to the filtrate. The difference between the two determinations represents the volatile sulphur.

L. DE K.

Rapid Estimation of Arsenious Oxide in Paris Green. By SAMUEL AVERY and H. T. BEANS (*J. Amer. Chem. Soc.*, 1901, 23, 485—486).—0.2—0.3 gram of the finely powdered sample is put into a 300 c.c. beaker, mixed with 25 c.c. of water, and hydrochloric acid added drop by drop until solution is just effected. After adding sodium carbonate solution until a slight permanent precipitate has formed, 2 or 3 grams of sodium potassium tartrate dissolved in water are added; the whole is diluted to 200 c.c., some solid sodium hydrogen carbonate and starch solution are added, and the arsenious oxide is titrated as usual with standard iodine. The slight blue colour caused by the copper does not sensibly interfere with the titration.

L. DE K.

Estimation of Cyanides and Cyanates. By ERNEST VICTOR (*Zeit. anal. Chem.*, 1901, 40, 462—465).—The following process is simpler than that of Mellor (this vol., ii, 202). A 10 per cent. solution of the mixture of cyanide and cyanate is prepared, and two quantities of 10 c.c. each are mixed with excess of $N/10$ silver nitrate in 100 c.c. flasks. One flask is then filled to the mark with distilled water, and the excess of silver titrated in an aliquot part of the filtrate by Volhard's thiocyanate process. To the other flask, some dilute nitric acid is added, by which the silver cyanate is dissolved, and the silver in the solution is estimated as before. The difference between the two titrations gives the cyanate. If carbonates are present, they are first removed by barium nitrate; the suggestion of Feldtmann and Bettel (*Proc. Chem. Metallurg. Soc. South Africa*, 1894—1897, 1, 274) to convert them into hydrogen carbonates by adding aqueous carbonic acid is not satisfactory, since the precipitation of silver carbonate is not altogether prevented. It is not necessary to work with solutions cooled to near 0° , for even at 25° a solution of cyanate remained constant in strength for about 3 hours.

M. J. S.

Estimation of Calcium Oxide in Soils. By EDUARD HOTTER (*Chem. Centr.*, 1901, ii, 235; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 4, 632—636).—Twenty grams of the dried and sifted soil are introduced into a 250 c.c. flask and heated for half an hour on the water-bath with 50 c.c. of 20 per cent. acetic acid; the solution is diluted to 250 c.c., and after 12 hours 200 c.c. of the clear liquid are siphoned off. The solution is precipitated with ammonium oxalate and the calcium oxalate converted into oxide by ignition. It is then purified by

dissolving it in very dilute nitric acid and reprecipitating the calcium in ammoniacal solution. When calculating the result, it may be assumed that 20 grams of the soil occupy a volume of 10 c.c. L. DE K.

Occlusion of Magnesium Oxalate by Calcium Oxalate. Solubility of Calcium Oxalate. By THEODORE W. RICHARDS, CHARLES F. McCAFFREY, and HAROLD BISBEE (*Zeit. anorg. Chem.*, 1901, 28, 71—89).—On precipitation of calcium oxalate in presence of magnesium salts, it is known that magnesium oxalate is always carried down, and it has already been suggested (*Abstr.*, 1900, ii, 472) that this occlusion is dependent upon a distribution of undissociated magnesium oxalate between the solution and the solid substance. In order to test this, experiments have been carried out in which the concentration of the undissociated magnesium oxalate was decreased by addition of a highly dissociated substance capable of forming complex ions with the magnesium or oxalic acid, and the amount of magnesium carried down with the calcium oxalate was determined. It was found that as the concentration of the undissociated magnesium oxalate was diminished, proportionately less of it was found in the precipitated calcium oxalate.

The authors recommend the following process for the separation of calcium from magnesium in solutions which should not be more than 1/50 normal with respect to magnesium. To the solution, an amount of ammonium chloride equivalent to 10 times the amount of magnesium present is added, and sufficient oxalic acid, to which some hydrochloric acid has previously been added, to completely precipitate the calcium. The solution is then boiled, and very dilute ammonia is added in small quantities at a time until the whole is exactly neutral to methyl-orange. A large excess of ammonium oxalate is now added, and the mixture, after standing for 4 hours, is filtered and washed with very dilute ammonium oxalate.

The solubility of calcium oxalate in pure water (0.0068 gram per litre at 25°; 0.00955 gram at 50°, and 0.0140 gram at 95°) is so large as to cause an appreciable error in exact analysis; in ammonium oxalate solution, it is very considerably less soluble.

J. McC.

Action of Sodium Thiosulphate on Solutions of Metallic Salts at High Temperatures and Pressures. By JOHN T. NORTON, jun. (*Amer. J. Sci.*, [iv], 12, 115—122).—At temperatures ranging from 140° to 200°, salts of nickel, cobalt, iron, zinc, lead, mercury, silver, copper, cadmium, antimony, and bismuth are completely precipitated as sulphides by sodium thiosulphate; manganese is only partially precipitated, and arsenic does not seem to be precipitated from an arsenate without the addition of acid. Salts of aluminium, chromium, titanium, zirconium, and thorium are completely precipitated as hydroxides, whilst beryllium is only partially precipitated as hydroxide. Salts of selenium and tellurium are reduced, and the elements are precipitated. In all cases, the precipitates are mixed with sulphur.

Quantitative experiments showed that whilst salts of aluminium and chromium are not completely precipitated by boiling during a reasonable time with sodium thiosulphate under atmospheric pressure,

a quantitative precipitation results when they are heated under 20 atmospheres pressure in a digester; in order to avoid high results, however, it is necessary to restrict the quantity of thiosulphate used. Salts of zirconium and titanium are precipitated quantitatively by boiling for a few minutes under atmospheric pressure. T. M. L.

[Precipitation of Zinc and Cadmium by Hydrogen Sulphide in Acid Solution.] By W. N. STULL (*J. Amer. Chem. Soc.*, 1901, 23, 508—514).—The equilibrium in the precipitation of zinc in acid solution by means of hydrogen sulphide is only reached after several hours, and at 20° zinc ceases to be precipitated when the solution contains about 5.25 per cent. of free sulphuric acid. Agitation and change of temperature within moderate limits are without appreciable influence on the rate of precipitation of zinc sulphide or on the final equilibrium.

Cadmium is quickly and completely precipitated at 20° by hydrogen sulphide from a solution containing any quantity of sulphuric acid. At 85°, the cadmium is completely precipitated when the solution contains up to 23 per cent. of sulphuric acid, but if the current of hydrogen sulphide is then stopped, the solution, as it loses this gas, redissolves the precipitate. The results indicate that the complete precipitation of cadmium as sulphide depends on the saturation of the solution with hydrogen sulphide, the temperature and concentration of the acid being only of secondary importance. J. McC.

Estimation of Small Quantities of Zinc in Iron-Spar. By J. FLATH (*Chem. Zeit.*, 1901, 25, 564—565).—Three to five grams of the powdered ore are dissolved in hydrochloric acid, the solution is diluted with 150—200 c.c. of water and mixed with ammonia in slight excess, 15 c.c. of glacial acetic acid are added, and a current of hydrogen sulphide is passed. Besides a little iron, the precipitate contains any zinc, copper, or lead which may have been present in the ore. The sulphides are washed on a filter with water containing a little hydrogen sulphide, and then dissolved in nitro-hydrochloric acid. The solution is mixed with 10 c.c. of dilute sulphuric acid (1:1), evaporated down, the residue dissolved in 100 c.c. of water, and the copper precipitated by boiling with 10—15 c.c. of solution of sodium thiosulphate (1:10). The filtrate is boiled with 5 c.c. of nitric acid, evaporated to a small bulk, and now freed from iron by a double precipitation with ammonia in the presence of bromine. The zinc is finally titrated in the ammoniacal solution as usual. L. DE K.

Volumetric Estimation of Zinc. By PERCY H. WALKER (*J. Amer. Chem. Soc.*, 1901, 23, 468—470).—The zinc solution is mixed with ammonium chloride and a large excess of ammonia and of sodium hydrogen phosphate is added. After filtering off from any insoluble phosphates, the ammonia is nearly neutralised with hydrochloric acid, which point is indicated by the solution becoming milky. After heating to 75°, more dilute acid is added drop by drop until the liquid is only faintly alkaline to delicate litmus paper. After waiting five minutes, the crystalline precipitate is collected on a filter and washed with cold water until the washings are practically free from chlorine;

the filter is returned to the beaker, the precipitate of zinc ammonium phosphate is dissolved in a known volume of standard sulphuric acid, and the excess of this titrated with standard alkali, using methyl-orange as indicator. One c.c. of normal acid represents 0.0327 gram of metallic zinc.

L. DE K.

A [Microchemical] Test for Indium. By P. KLEY (*Chem. Zeit.*, 1901, 25, 563).—The best test for indium is the formation of the double chloride of indium trichloride and rubidium chloride. It forms colourless crystals of an octahedral character, which, however, polarise well and belong to the rhombic system. Directions are given for the separation of indium and the formation of the chloride, by which as little as 0.00024 mgr. of indium can be detected. The microchemical reaction for indium described by Hysse (*Abstr.*, 1900, ii, 246) is untrustworthy.

R. H. P.

Modified Williams' Method for Estimating Manganese. By RANDOLPH BOLLING (*J. Amer. Chem. Soc.*, 1901, 23, 493—496).—The modification consists in removing the silica by means of 10 c.c. of hydrofluoric acid, which are added when dissolving the sample of iron or iron ore in nitric acid. The liquid is then heated, as usual, with strong nitric acid and potassium chlorate, and the manganese dioxide collected on an asbestos filter pad. Owing to the absence of silica, it may be rapidly freed from the acid solution by washing. The asbestos is now returned to the beaker, and the precipitate dissolved by adding 50 c.c. of standardised solution of iron sulphate (20 grams of the pure salt, 200 c.c. of sulphuric acid, and water to make up to 2 litres). The excess of ferrous iron is then titrated with potassium permanganate solution, 1 c.c. of which represents 0.0056 gram of iron.

As it is doubtful whether all the manganese is really in the state of dioxide, and also on account of the presence of carbon in the samples and the use of asbestos, the author prefers checking his solutions by means of a sample of iron the manganese of which has been accurately estimated, for example, by Gibbs' pyrophosphate method.

L. DE K.

Volumetric Estimation of Chromium Oxide in Chromium Oxide Mordants. By R. HARTMANN (*Chem. Zeit.*, 1901, 25, 564).—The following method is recommended. About 1 gram of the mordant (chromium acetate of sp. gr. 1.17) is diluted with 10—15 c.c. of water, and mixed with aqueous sodium hydroxide until the precipitate has redissolved. The liquid is heated on the water-bath, and sodium dioxide added until the solution has assumed a bright yellow colour. After evaporation to dryness, the mass is dissolved in 500 c.c. of water, excess of dilute sulphuric acid added, and the chromic acid estimated as usual by means of ferrous ammonium sulphate and potassium permanganate. If the mordant should contain other organic matter, this must be first destroyed by treatment with nitric acid, or potassium chlorate and hydrochloric acid, and subsequent evaporation with sulphuric acid.

L. DE K.

Use of Diphenylcarbazine for the Detection of Chromic Acid in Cotton Dyed with Chrome Yellow. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1901, [iii], 25, 761—762).—The fibre is decolorised by

treatment with potassium hydroxide, and the test applied as previously described (Abstr., 1900, i, 627). N. L.

Alkaline Waters from the Chalk. By WALTER W. FISHER (*Analyst*, 1901, 26, 202—208).—Tables are given containing a large number of analyses of well waters from different parts of England. Those obtained from uncovered chalk wells show no alkalinity to speak of after boiling, but when the chalk is covered with a layer of clay, the alkalinity becomes very marked, owing to the presence of alkali carbonate. The sodium carbonate is most likely formed by the action of sodium silicate from the clay on the calcium hydrogen carbonate contained in the water, but the subject is being further investigated. L. DE K.

Estimation of Carbon Dioxide in Water. By JOSEPH W. ELLMS and JAY C. BENEKER (*J. Amer. Chem. Soc.*, 1901, 23, 405—431).—A lengthy investigation as to the respective merits of the original Pettenkofer method, Trillich's modification of the same, and the Lunge-Trillich or Seyler's method for the estimation of carbon dioxide in its various forms.

On account of the ease and rapidity of manipulation, the non-interference of magnesium salts and its greater accuracy, the last process is to be preferred for the estimation of carbon dioxide in waters.

L. DE K.

[Improvements in the] Estimation of Ammonia and Nitric and Nitrous Acids in Drinking Waters. By LUDWIG W. WINKLER (*Chem. Zeit.*, 1901, 25, 586—587. Compare Abstr., 1899, ii, 805).—*Ammonia*.—The Rochelle salt solution required is now prepared by dissolving 50 grams of the salt in 100 c.c. of warm water, and adding 5 c.c. of the author's Nessler solution; this not only preserves the solution, but also frees it from traces of ammonia. After a few days, it should be filtered through cotton-wool. Ordinary water free from ammonia may be used instead of distilled water for the comparison test.

Nitric Acid.—The recommendation is now made that to the sample and to the comparison water about 0.03 gram of solid brucine should be added, and dissolved by means of a drop of sulphuric acid before adding the bulk of the acid. Instead of using ordinary flasks, glass tubes holding 50 c.c., and having a diameter of 3 cm., are recommended, and the colours are compared as in the Nessler test.

Nitrous Acid.—The whole of the 5 grams of potassium hydrogen carbonate, in crystals, is added in one quantity; after 1 minute, 0.2 gram of potassium iodide is added, and the liberated iodine titrated after 5 minutes. Sterilised starch water without any preservative is recommended. L. DE K.

Estimation of Sulphuric Acid in Drinking Waters. By C. HARTLEB (*Chem. Centr.*, 1901, ii, 320; from *Pharm. Zeit.*, 46, 501—502).—After a preliminary test, 100 c.c. of the sample are boiled with 10 c.c. or more of *N/10* barium chloride solution. The excess of the latter is titrated by adding a solution containing 9.8 grams of potassium chromate per litre. The end reaction is noticed by testing a few drops of the liquid with *N/10* silver nitrate. The checking of the chromate and the barium solutions is also effected with the aid of silver

nitrate as indicator. The sulphuric acid is calculated from the difference between the potassium chromate consumed before and after adding the barium chloride to the water. L. DE K.

Estimation of Sulphuric Acid in Natural Waters. By LUDWIG W. WINKLER (*Zeit. anal. Chem.*, 1901, 40, 465—469).—A very rapid estimation of sulphuric acid in potable waters, with sufficiently close approximation for hygienic purposes, can be made by converting the method of Andrews (Abstr., 1890, 414) into a colorimetric one. One hundred and fifty or 200 c.c. of the water are acidified with 5—10 drops of hydrochloric acid and 0.1—0.2 gram of pure barium chromate is added; the liquid is heated to boiling, then completely cooled, and mixed with a very small excess of sodium hydroxide. It is then filtered through dry double filters, the first turbid portion rejected, and 100 c.c. of the clear filtrate are compared with 100 c.c. of alkaline water to which potassium dichromate solution is added from a burette. The dichromate solution contains 1.839 gram per litre: 1 c.c. is equivalent to 0.001 gram of sulphur trioxide. A correction of 0.7 c.c. is to be made to allow for the solubility of barium chromate in dilute alkali.

M. J. S.

Refractometric Method of Determining Alcohol and Solid Matter in Beer. By ARTHUR R. LING and THOMAS HENRY POPE (*J. Fed. Inst. Brewing*, 1901, 7, 170—181).—The authors have determined the amount of solid matter and alcohol in a number of English beers of various kinds by (1) the ordinary distillation method and (2) Tornöe's refractometric method, which dispenses with distillation, the measurements made being (a) the sp. gr. of the beer at a normal temperature (17.5°) which is obtained by the use of very accurate hydrometers reading direct to 0.0001; (b) the refractive index of the beer for sodium light at the same normal temperature. The latter magnitude is obtained with the help of a Hallwachs' double prism, which contains the beer in one compartment and water in the other, and is mounted on a spectrometer stand designed by Tornöe. The instrument is so constructed that only one reading is necessary to give the value of double the angle of deviation suffered by a ray of sodium light passing in the limiting position from water into beer. From this angle, the index of refraction of the beer may, if necessary, be calculated, but tables have been constructed which give the percentage of alcohol and extract in the beer when the values of the angle and of the sp. gr. are known. This process, which can be carried out in about 10 minutes, gives results agreeing well with those obtained by the ordinary distillation method, the agreement being equally good in the case of beers brewed with large proportions of malt substitutes. T. H. P.

Sulphurous Acid in Wines. By G. PATUREL (*Ann. Agron.*, 1901, 27, 305—317).—After criticising existing methods, the following process is recommended. Fifty c.c. of the sample of red wine are introduced into a generating flask and mixed with 5 c.c. of dilute sulphuric acid (1:2). A slow current of carbon dioxide, which is first passed through a washbottle containing a solution of sodium hydrogen carbonate, is transmitted through the wine and is then made to bubble

through 50 c.c. of recently boiled water containing a little starch solution. Over the beaker containing the liquid is placed a burette filled with solution of iodine of such a strength that 1 c.c. represents exactly 0.0005 gram of sulphur dioxide; the iodine is constantly added in slight excess while the gas is passing. When, finally, no further discoloration takes place, the experiment is stopped and the number of c.c. of iodine consumed is noted. The operation rarely takes more than 30 minutes.

The process shows only the free sulphur dioxide and not that portion which has combined with any aldehyde present; the latter must be estimated by the distillation process. L. DE K.

New Indicator for Determining the Total Acidity of Wines. By E. G. RUNYAN (*J. Amer. Chem. Soc.*, 1901, 23, 402—405).—The author uses the indicator proposed by Lachaux which is prepared as follows: 3.1 gram of corallin (rosolic acid) are dissolved in 150 c.c. of 90 per cent. alcohol and carefully neutralised; to this is then added 0.5 gram of malachite green dissolved in 50 c.c. of alcohol. This indicator turns a purple colour with alkalis and is changed to green by acids. Ten c.c. of the sample of wine are diluted with 300 c.c. of boiling water, boiled for a moment to expel carbon dioxide, and cooled to 75°; 10 drops of the indicator are added, and then an excess of *N*/10 sodium hydroxide. The excess of alkali is then titrated by means of *N*/10 acid, the change in colour being best observed by transmitted light. The indicator answers also for estimating the acidity of beet molasses, vinegars, and ciders. L. DE K.

Estimation of Volatile Acids and Chlorides in Wines. By ALBERT KLEIBER (*Chem. Centr.*, 1901, ii, 240; from *Schweiz. Wochschr. Pharm.*, 39, 295—300).—The German method of distilling 100 c.c. of wine in a current of steam and collecting 200 c.c. of distillate for titration is sufficiently accurate; nothing is gained by increasing the volume of the distillate. When 100 c.c. of wine are distilled in such a manner that 68 c.c. are collected in about 20 minutes, the distillate contains the bulk of the volatile acids. After adding water to make up to 100 c.c., 50 c.c. are used for titration.

To estimate chlorine, the wine is neutralised with soda, evaporated to dryness, and the residue charred. The mass is then extracted with water, and the filtrate neutralised with nitric acid and titrated with silver nitrate as usual. L. DE K.

Elimination and Estimation of Water in Oils, Fats, and Waxes. By CHARLES B. DAVIS (*J. Amer. Chem. Soc.*, 1901, 23, 487—488).—In order to prevent loss by foaming or spirting when drying fats or oils containing water, the author uses a wide-mouth, glass-stoppered weighing bottle, which is half filled with a coil of thick filter paper. The whole is first dried in the air-oven at 110° and weighed; a sufficiency of the sample is introduced, and, after ascertaining its weight, the whole is again dried at 110° and reweighed. As the fat is absorbed by the paper, the drying proceeds quietly; samples liable to oxidation should be dried in a current of carbon dioxide or hydrogen.

Small samples may be dissolved in ether, the solution poured on to the filter paper, the ether evaporated at a low temperature, and the drying afterwards carried out at 110°.

L. DE K.

Determination of the Saponification Number of Fats. By OTTO SCHMATOLLA (*Chem. Centr.*, 1901, ii, 239—240; from *Apoth. Zeit.*, 16, 425).—Five grams of the oil are boiled with 20 c.c. of normal potassium hydroxide solution until a stiff paste is obtained, 20 c.c. of dilute alcohol are added, and the whole warmed until the mass becomes soft. After dissolving the mass in as little dilute alcohol as possible, 20 c.c. of strong brine are added, and the whole heated, cooled, and, when cold, filtered through linen. The soap is well pressed and once more treated with brine. The united salt solutions are filtered through paper, and the excess of alkali titrated with normal hydrochloric acid, methyl-orange being used as indicator. The difference represents the amount of potassium hydroxide absorbed by the fat.

L. DE K.

Cryoscopic Distinction between Butter and Margarine. By W. PESCHGES (*Arch. Pharm.*, 1901, 239, 358—363).—The distinction between butter and margarine, by means of cryoscopic determinations of the molecular weight in benzene (Pouret, *Abstr.*, 1899, ii, 710), is found by the authors not to be valid. The values for the molecular weights obtained by Pouret, namely, 640 for butter and 840 for margarine, do not agree with those calculated from the Köttstorfer saponification numbers, which give 716—763 for butter, and 840—875 for margarine. When the molecular weights are determined by the boiling point method in benzene, still lower values (387—413) are found for the molecular weight of butter. With ether as solvent, the molecular weight is the same as that calculated from the Köttstorfer numbers. The latter, however, can be determined with far greater accuracy than the molecular weight.

K. J. P. O.

Estimation of Urea in Urine. By OTTO FOLIN (*Zeit. physiol. Chem.*, 1901, 32, 504—514).—The urine (3 c.c.) is boiled with 20 grams of hydrated magnesium chloride and 2 c.c. of concentrated hydrochloric acid in a small reflux apparatus for some 30 minutes. After careful dilution, 7 c.c. of 20 per cent. sodium hydroxide are added to liberate magnesium hydroxide, and the ammonia distilled over in the usual way; this operation requires, as a rule, about 60 minutes. Corrections must be made for the ammonia contained in the magnesium chloride, and also for that originally present in the urine.

The Mörner-Sjöquist method for obtaining from urine filtrates which contain all the urea is preferable to the Pflüger-Gumlich phosphotungstic acid method.

It appears probable that the methods described above may be used for estimating urea in urine without the previous removal of other nitrogenous substances.

J. J. S.

Formalinsulphuric Acid as a Reagent for Alkaloids. By CURT ELIAS (*Chem. Centr.*, 1901, ii, 57; from *Pharm. Zeit.*, 1901, 46, 394—441).—The author has applied the formalinsulphuric acid test to a number of other alkaloids (compare Wirthle, this vol., ii, 363). In

addition to morphine, codeine and apomorphine gave the violet colour. Narcotine was also coloured distinctly violet; the colour became olive-green, and finally yellow. Papaverine, not absolutely pure, out giving with sulphuric acid a passing faint violet, assumed a wine-red colour which, after some time, became yellow round the edges, and then turned first a dirty brownish-red, and afterwards dark orange. Thebeine, narceine, quinine, cinchonine, arecoline, physostigmine, pilocarpine, caffeine, cocaine, brucine, strychnine, hyoscine, atropine, and veratrine only gave the ordinary reactions.

L. DE K.

Assay of Coca. By WILLIAM R. LAMAR (*Amer. J. Pharm.*, 1901, 73, 125—131).—Twenty-five grams of the powdered leaf are placed into a suitable vessel, moistened with 25 c.c. of 2 per cent. solution of ammonia, and allowed to macerate for half an hour, the vessel being well covered. The mass, which should still have a distinct odour of ammonia, is now gradually mixed with 75 c.c. of petroleum, the jar is again covered and left for an hour, stirring at intervals of 10 or 15 minutes. The mass is now transferred to a cylindrical percolator of about 500 c.c. capacity, slightly plugged with absorbent cotton. The percolation, which should proceed at the rate of 6 or 8 drops per minute, is continued until about 450 c.c. of petroleum have been collected. The percolate is then transferred to a large separating funnel, and shaken for 10 minutes with 25 c.c. of *N*/10 hydrochloric acid. When the two layers have separated, the acid is drawn off, and the shaking with acid is twice repeated. The united acid liquids, which contain the alkaloids, are shaken in another separator with 20 c.c. of ether to remove oily and colouring matters; this is repeated in a fresh separator, using 15 c.c. of ether. The purified liquid is transferred to a third separator; to it are added the washings obtained by shaking the first lot of ether with two portions of 5 c.c. of water, and using the same for washing the second lot of ether.

The aqueous liquid is now rendered slightly alkaline by adding 8 to 9 c.c. of 2 per cent. ammonia, and then shaken three times in succession with respectively 40, 30, and 30 c.c. of ether; each time the aqueous layer is drawn off into a clean separator, the ether is emptied into a tared beaker, and the separator is rinsed with ether, which is then used for the next extraction. When the ether has evaporated, the residue is dried for 3 hours at 60° and weighed. The alkaloids so obtained should be beautifully crystalline in appearance and almost colourless.

L. DE K.

Assay of Opium. By A. B. STEVENS (*Pharm. Arch.*, 1901, 4, 81—86).—A modification of the U.S.P. method. Four grams of opium powder are mixed in a mortar with 1.5 grams of calcium oxide and 10 c.c. of water to a paste; another 19 c.c. of water are added, and the whole stirred frequently for half an hour. After filtering, 15 c.c. of the liquid are transferred to a 60 c.c. bottle, 4 c.c. of alcohol and 10 c.c. of ether are added, and the mixture is well shaken; 0.5 gram of ammonium chloride is added, and the mixture frequently shaken for half an hour.

After 12 hours, the ethereal layer is poured into a small funnel, the neck of which has been closed with a piece of absorbent cotton. The

bottle is rinsed with 10 c.c. of ether, and when this has passed through, the contents of the bottle are poured into the funnel. Without trying to remove all the crystals from the bottle, this is washed with water saturated with morphine until the washings are colourless. When the crystals have drained, the funnel is placed in the bottle, the cotton is lifted by means of a small glass rod drawn out to a curved point, and the crystals are rinsed into the bottle by means of 12 c.c. of *N*/10 sulphuric acid, using the cotton on the end of the rod to detach any adhering crystals. The cotton is put into the flask, the stopper inserted, and the whole shaken until the morphine is dissolved. The solution is transferred to a 100 c.c. flask, and the bottle and funnel washed with water in sufficient quantity to make the acid solution up to exactly 100 c.c. Fifty c.c. of this are put into a 100 c.c. flask, and Wagner's reagent is added in small quantities until the precipitate has settled and a clear, dark-red solution is obtained, when the whole is diluted to the mark. Fifty c.c. of the filtrate (0.5 gram of opium) are now decolorised by means of a 10 per cent. solution of sodium thiosulphate, and the excess of acid is then titrated with *N*/10 potassium hydroxide, using phenolphthalein as indicator. The number of c.c. of *N*/10 acid consumed by 1 gram of opium multiplied by 3.007 gives the percentage of morphine. This result should be corrected by adding 1.12 per cent. of morphine lost during the estimation.

Instead of the titration process being used, the crystals may also be dried and weighed, as they may be taken to be practically pure.

L. DE K.

Differentiation between Albumins, Syntonins, Albumoses, and Peptones of Muscular Tissue. By BILTÉRYST (*Ann. Chim. anal. appl.*, 1901, 6, 241—243).—The author has prepared soluble albumins, syntonins, albumoses, and peptone from the muscular tissue of the ox, and gives a table showing their different behaviour towards reagents.

Solubility in water. Albumins are partly soluble, the others are dissolved. *Solubility in alcohol of 95 per cent.* Only peptone is fairly soluble. *Action of heat.* Albumins only are coagulated. *Acetic acid.* Albumins and syntonins only are precipitated. *Hydrochloric acid.* Albumins and syntonins only are precipitated. *Nitric acid.* Albumins are precipitated, syntonins also, but the precipitate redissolves on heating; albumoses give a slight opalescence disappearing on heating, peptone is not precipitated. *Potassium ferrocyanide in the presence of acetic acid.* Albumins and syntonins are precipitated, albumoses give a faint turbidity, peptone is not affected. *Ammonium sulphate to saturation.* Albumins, syntonins, and albumoses only are precipitated. *Biuret reaction.* Peptone only gives a rose coloration, also in alcoholic solution.

L. DE K.

General and Physical Chemistry.

Sensitiveness of the Reactions based on Spectrum Analysis. By W. SCHULER (*Ann. Phys.*, [iv], 5, 931—942).—For the metals in the first two groups of Mendeléeff's system, the sensitiveness of flame and spark reactions diminishes with increasing atomic weight. For the salts of a given metal, the sensitiveness diminishes with increasing atomic weight from chloride to iodide, and in the oxy-salts with increasing number of oxygen atoms. When two metals are present, they are mutually affected, but the sensitiveness of a light metal is much more diminished than that of a heavy metal. When hydrogen chloride or chloroform vapour is mixed with the burning gas, the intensity of the flame spectrum of a metal is seriously diminished, the effect of chloroform vapour being more marked than that of hydrogen chloride (compare Smithells, *Phil. Mag.*, 1895, 39, 122). J. C. P.

Spectra of Hydrogen, and some of its Compounds. By JOHN TROWBRIDGE (*Phil. Mag.*, 1901, [vi], 2, 370—379. Compare Abstr., 1900, ii, 701).—The author's experiments lead him to the conclusion that pure dry hydrogen is an insulator, and that the passage of electricity through hydrogen, nitrogen, oxygen, and their gaseous compounds is conditioned by the water vapour present. The passage of the current is electrolytic in character; for example, when a strong, steady current is passed between pure copper electrodes in rarefied hydrogen (not perfectly dry), copper is deposited in a lustrous state on the walls round the negative electrode, and an olive-green oxide of copper is deposited on the walls round the positive electrode. Although the author has not obtained the spectra of hydrogen apart from water vapour and hydrocarbons, the brilliancy of the light of hydrogen tubes diminishes as the dissociation of water vapour proceeds and the resistance of the tube increases. J. C. P.

Spectrum of Cyanogen. By EDWARD C. C. BALY and H. W. SYERS (*Phil. Mag.*, 1901, [vi], 2, 386—391).—A description of experiments confirmatory of Smithells' view (this vol., ii, 366) that the Swan spectrum is the spectrum of carbon monoxide. In particular, it has been shown that a cyanogen spectrum can be obtained without a trace of the carbon spectra. To get the cyanogen in a state of purity, the gas obtained by heating mercuric cyanide was frozen by means of liquid air, and any non-condensable residue pumped off. The pure cyanogen obtained by volatilisation of the frozen mass gave a beautiful spectrum, with equidistant flutings through the red and yellow. The admission of air or oxygen into the tube was at once followed by the appearance of the carbon spectra. The rapid polymerisation of the cyanogen under the influence of the discharge was a source of trouble, but this was got over by passing a constant slow stream of the gas into the tube. It was further necessary to observe the discharge 'end on,' on account of the deposition of paracyanogen on the walls of the tube. J. C. P.

Luminescence Spectra of the Rare Earths. By F. BAUR and R. MARC (*Ber.*, 1901, **34**, 2460—2466).—The luminescence spectra attributed by Muthmann and Baur (*Abstr.*, 1900, ii, 544) to yttrium, gadolinium, and lanthanum, are now shown to be produced by small quantities of erbium, neodymium, and praseodymium present as impurity. The oxides and salts of yttrium, gadolinium, and lanthanum have, when pure, no discontinuous spectrum. The authors have recorded all the lines and bands observed for solutions of erbium, neodymium, and praseodymium in calcium oxide, yttria, and the corresponding sulphates. J. C. P.

Photochemical Decomposition of Hydrogen Iodide: a Contribution to the Knowledge of Sensitising Action. By JOHANNES PINNOW (*Ber.*, 1901, **34**, 2528—2543. Compare this vol., ii, 368).—When solutions of potassium iodide and sulphuric acid are kept in the dark, the rate of oxidation of the hydrogen iodide, as measured by titration with thiosulphate, does not increase proportionately to the concentration of the sulphuric acid; when, however, the solutions are exposed to sunlight, the amount of iodine liberated is proportional to the sulphuric acid, provided the potassium iodide concentration is not above 1 gram per litre; the accelerating influence of light is most evident in the more dilute solutions of potassium iodide. The liberation of iodine, both in the dark and in the light, is about twice as rapid when hydrochloric acid takes the place of sulphuric acid. The liberation of iodine from a mixture of potassium iodide and phosphoric acid is only slightly accelerated by light. The oxidation of a mixture of potassium iodide and sulphuric acid is accelerated, generally by quinine, always by acridine, the fluorescence in both cases being diminished. Excess of sulphuric acid, however, both restores the fluorescence and checks the accelerating influence of the sensitiser. J. C. P.

The Diazotype Process in Photographic Printing. By ARTHUR G. GREEN, CHARLES F. CROSS, and EDWARD J. BEVAN (*Ber.*, 1901, **34**, 2495).—A correction of Ruff and Stein's views (this vol., i, 619) as to the authors' work in the same direction (*Abstr.*, 1891, 138). W. A. D.

Determination of the Dielectric Constants of some Substances of the Pyridine and Piperidine Series by Drude's Method. By R. LADENBURG (*Zeit. Elektrochem.*, 1901, **7**, 815—817).—The determinations were made by Drude's electrical oscillation method, and gave the following values of the dielectric constants at 22°:—Pyridine, 12·56; α -picoline, 9·46; β -picoline, 10·71; 2-ethyl pyridine, 8·56; α -conyrine (2-propylpyridine), 7·36; 2-isopropylpyridine, 7·68; 2-methyl-5-ethylpyridine, 7·95; 2:6-dimethylpyridine, 7·23; 2:4:6-trimethylpyridine, 6·64; piperidine, 4·33; α -pipecoline, 3·55; d -coniine, 3·03; 2-isopropylpiperidine, 2·95; 2:4:6-trimethylpiperidine, 3·06; 1-methylpiperidine, 2·90; 1-ethylpiperidine, 2·49; 1-isopropylpiperidine, 2·26; 1:2-dimethylpiperidine, 2·17.

The introduction of an alkyl group diminishes the dielectric constant, the diminution being greatest in the 1-position and least in the

4-position ; it also increases with the number of carbon atoms in the side chain. T. E.

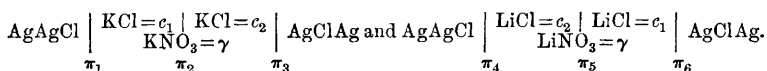
Electrical Properties of Chromium during Dissolution in Acids. By EBERHARD BRAUER (*Zeit. physikal. Chem.*, 1901, 38, 441—486).—The dissolution of 'active' chromium is attended by a remarkable periodicity in the rate of evolution of hydrogen, whilst active chromium also exhibits changes in its electric potential as the current produced by a cell of active chromium and platinum immersed in acid periodically varies. The author describes apparatus by which both these variations can be simultaneously studied ; a cell of active and inactive chromium in hydrochloric acid was employed, and the variations of hydrogen evolution and of current strength produced oscillations of two reflecting mirrors, whereby two permanent records on photographic paper were obtained in juxtaposition. It was found that the two variations were intimately connected, perfectly analogous curves being obtained for both, although evidence of variations in the electrical properties was obtained when the evolution of hydrogen was apparently constant. The influence of temperature was studied ; no periodicity was observed at 6°, it was very marked at 20°, and an increase to 31° caused a great increase in the frequency. The effect of variation of concentration of the acid was also investigated ; the frequency was found to increase with concentration, but to be no longer apparent when the acid was too strong. A cell was also employed in which a current of the acid was maintained, so that variations of composition at the electrodes were avoided ; in some cases, a sufficiently rapid flow of acid caused a cessation of the periodicity. It was found that a piece of pure chromium was inactive, but that activity was induced by rubbing with a piece of cadmium. Slight activity was also occasioned by the addition of sulphides or arsenic to the acid, this addition having further very great influence on the periodicity of active chromium. The author considers that the explanation of these phenomena is to be looked for in the variations of *E.M.F.* associated with the different oxidation stages of chromium (Luther, this vol., ii, 301. Compare Hittorf, *Abstr.*, 1898, ii, 363 ; 1900, ii, 127 ; Ostwald, *Abstr.*, 1900, ii, 730 ; 1901, ii, 24). L. M. J.

Equilibria at Gas Electrodes. By EMIL BOSE (*Zeit. Elektrochem.*, 1901, 7, 817—821).—The chemical reactions occurring at gas electrodes are usually complicated by secondary changes. The hydrogen electrode is free from these, but chlorine reacts with water thus, $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HClO}$, and the final *E.M.F.* of the chlorine electrode is not reached until the equilibrium represented by this equation is established. The *E.M.F.* of the oxygen electrode increases gradually for days, finally reaching a value which probably corresponds with the establishment of the equilibrium $\text{H}_2\text{O} + \text{O} \rightleftharpoons \text{H}_2\text{O}_2$. The author considers that it is doubtful whether the peroxide formed is hydrogen peroxide, or an isomeric substance, or a higher peroxide. When the electrolyte used is sulphuric acid, a small quantity of persulphuric acid must also be produced, and this must be in equilibrium with the hydrogen peroxide and oxygen. T. E.

Experimental Contribution to the Theory of the Drop Electrode. By J. BERNSTEIN (*Zeit. physikal. Chem.*, 1901, **38**, 200—204).—A cell containing two mercury electrodes (one being a drop electrode) was connected with a capillary electrometer. The movements of the meniscus in the electrometer and the formation and fall of the mercury drop in the cell were photographically recorded on the same plate. The current corresponding with the fall of each drop is thereby shown to be produced at the very moment of separation of the drop. The meniscus of the electrometer reached its point of maximum displacement 0.034 sec. after it began to move. The observation is interpreted according to Ostwald's (Abstr., 1888, 886) and Paschen's (Abstr., 1890, 552, 1036) views. J. C. P.

Nomenclature of the Ions. By JAMES WALKER (*Chem. News*, 1901, **84**, 162—163).—A system of names is suggested for the material of the ions as distinguished from the particles themselves. For positive radicles, the termination 'ion' is added to the stem, and, where necessary, a Greek numeral is prefixed to indicate the valency of the metal: for example, hydrion (H^+), barion (Ba^{++}), monomercurion (Hg^+), triferrion (Fe^{+++}). For negative radicles, the names are obtained by substituting 'anion,' 'osion,' 'idion,' for 'ate,' 'ite,' and 'ide' respectively; for example, hydroxidion (OH^-), sulphosion (SO_3^{--}), sulphanion (SO_4^{--}), carbanion (CO_3^{--}), chloridion (Cl^-). Terms such as 'chlorine ions' or 'chloridion molecules' should be used in speaking of the ions as particles, but 'chloridion' in speaking of the substance which constitutes them. J. C. P.

Influence of the addition of a Salt with one similar Ion on the E.M.F. of Electrolytic Cells. A Contribution to the Knowledge of the Behaviour of Strong Electrolytes. By OTTO SACKUR (*Zeit. physikal. Chem.*, 1901, **38**, 129—162).—The equation given by Abegg and Bose (Abstr., 1900, ii, 127) for the influence of the addition of a salt with one similar ion on the *E.M.F.* of electrolytic cells has been arrived at thermodynamically by the author. In an experimental investigation of the subject, he has measured the *E.M.F.* of the cells



By adding the *E.M.F.* of these two cells, the potential difference, π_5 , is found, for $\pi_1 + \pi_3 + \pi_4 + \pi_6 = 0$, and π_2 is negligible, the rates of migration of the potassium and chlorine ions being almost equal. The values thus obtained for π_5 agree excellently with those calculated by the equation $\pi_5 = -RT/\epsilon \cdot (u-v)/(u+v) \cdot \log_e(k_1/k_2)$, where k_1 and k_2 are the conductivities of the lithium salt solutions. An excellent agreement with theory is also obtained when hydrochloric acid and nitric acid take the place of lithium chloride and lithium nitrate in this system.

On the basis of the law of mass action, with the help of the *E.M.F.* of the potassium salt cell described above and the conductivities of the two solutions, the degree of dissociation in the mixed potassium

chloride and nitrate solution has been calculated. The results lead to the conclusion either that the law of mass action is invalid for strong electrolytes, or that the ionic velocities alter with the concentration (compare Jahn, Abstr., 1900, ii, 522, 707; this vol., ii, 299, 491). Conductivity measurements in mixed solutions show the inadequacy of Jahn's view that the deviations of strong electrolytes from the law of mass action are due to the increase with concentration of the ionic velocities (compare also Arrhenius, this vol., ii, 144, 435; Nernst, this vol., ii, 370; Leffeldt, this vol., ii, 433; Sand, this vol., ii, 303).
J. C. P.

Electrolytic Reduction of Nitrites. By BER SÜLER (*Zeit. Elektrochem.*, 1901, 7, 831—842 and 847—855).—The analytical methods used for the determination of hydroxylamine, ammonia, and nitrite in presence of each other are fully described. Hydroxylamine is determined by boiling with Fehling's solution, the reaction being $2\text{NH}_2\cdot\text{OH} + 4\text{CuO} = \text{N}_2\text{O} + 2\text{Cu}_2\text{O} + 3\text{H}_2\text{O}$. Ammonia is determined by distillation in the usual way, copper sulphate being added to the alkaline liquid in order to destroy hydroxylamine. Nitrite is determined by distilling the solution with sodium hydroxide and ferrous sulphate, the nitrites and hydroxylamine being reduced by this treatment to ammonia.

In the electrolytic experiments, a solution of potassium nitrite was placed in a porous cell containing a cathode of zinc, the anode was of platinum immersed in a concentrated solution of sodium or potassium carbonate. The mean results obtained are as follows:

(a) Cathodic current density, 0.02 ampere per sq. cm. Temperature, 14—17°.

| Concentration of cathode solution. | Current efficiency (per cent.). | |
|---------------------------------------|---------------------------------|-----------------|
| | $\text{NH}_2\cdot\text{OH}$. | NH_3 . |
| 5 per cent. | 54.3 | 32.5 |
| 10 " | 21.0 | 54.2 |
| 15 " | 6.6 | 75.5 |
| 25 " | 2.0 | 75.4 |

(b) Temperature, 14—25°. Concentration, 5 per cent.

| Current density at cathode. | Current efficiency (per cent.). | |
|--------------------------------|---------------------------------|-----------------|
| | $\text{NH}_2\cdot\text{OH}$. | NH_3 . |
| 0.02 | 54.3 | 32.5 |
| 0.05 | 33.1 | 13.8 |
| 0.1 | 27.6 | 10.3 |

(c) Concentration, 5 per cent. potassium nitrite; current density at cathode, 0.02 ampere per sq. cm.

| Temperature. | Current efficiency (per cent.). | |
|--------------|---------------------------------|-----------------|
| | $\text{NH}_2\cdot\text{OH}$. | NH_3 . |
| 0—2° | 59.5—60 | 31—35 |
| 45—50 | 16.8—18.4 | — |
| 75—90 | 7.6—9.6 | — |

T. E.

[Electrochemical Reduction.] By FRITZ HABER (*J. pr. Chem.*, 1901, [ii], 64, 289—293).—Polemical: a reply to Binz (this vol., i, 593).
K. J. P. O.

Determination of the Constitution of Complex Salts by Electrolytic Transference. By E. RIEGER (*Zeit. Elektrochem.*, 1901, 7, 863—868 and 871—876).—The author has made determinations of the electrolytic transference of the ions of the following salts: potassium copper sulphate, potassium silver iodide, potassium mercuric iodide, potassium mercuric cyanide, potassium zinc cyanide, potassium cadmium cyanide, potassium ferrous and ferric oxalates. In all of them, the metal migrates towards the anode, although only partially in the case of the first-named salt. The presence of complex anions, indicated by this behaviour, is confirmed by the small conductivity of the solutions, which is always less than the sum of the conductivities of the constituents.
T. E.

Constitution of Inorganic Compounds. By ALFRED WERNER and CH. HERTY (*Zeit. physikal. Chem.*, 1901, 38, 331—352).—The authors uphold the views previously expressed (*Abstr.*, 1897, ii, 100) against the objections raised by Petersen (*Abstr.*, 1897, ii, 302). They maintain that the number of ions into which the metal-ammonia (and similar) compounds are dissociated can be ascertained from the electrical conductivity. The compounds examined by Petersen all undergo change when in contact with water, and the conductivities found by him are throughout too high. The electrical conductivities of several ethylenediamine-cobalt salts have been determined and compared with those of the corresponding ammonio-salts, and it has been found that by the substitution of ethylenediamine for ammonia the molecular conductivity is diminished. It was noticed that many of these compounds were considerably decomposed in the conductivity cell, and this was found to be due to the platinum sponge on the electrodes, which causes decomposition with evolution of gas and increase of molecular conductivity with the time. This has been observed with oxalotetramminocobalt bromine, dithiocyanodiethylenediamminocobalt nitrate, and the corresponding diisothiocyanosalt.

In the case of those salts with complex ions which suffer hydration in aqueous solution, the conductivity increases with the time. From the conductivity of the solution immediately after preparation, the number of ions into which it dissociates can be inferred, and the result so obtained can be confirmed by determination of the lowering of the freezing point. If the solution be kept at 0°, the conductivity remains constant for a considerable time. In this way, it is shown that the following salts dissociate, giving two ions: 1:6-dichlorodiethylenediamine-cobalt chloride (green), the same 1:2-salt (violet), and the corresponding nitrates.

The results obtained with the non-conducting salts are not in agreement with those found by Petersen. The fresh solutions have a very small conductivity, which increases with the time, but from the initial low value it is to be concluded that in the undecomposed state these salts do not dissociate. This has been experimentally proved for

cis- and *trans*-dichlorodiamminoplatinum (platosemidiamminochloride and platosamminochloride), *cis*-dichloropropylenediamminoplatinum, *cis*-dichloroethylenediamminoplatinum, and *cis*- and *trans*-tetrachlorodiamminoplatinum (platinisemidiamminochloride and platinamminochloride).

By determining the depression of the freezing point, it has been proved that hexamminocobalt chloride gives 4 ions, nitropentamminocobalt chloride gives 3 ions, nitroaquotetramminocobalt chloride gives 3 ions, and dinitrotetramminocobalt chloride gives 2 ions. J. McC.

Law of Physico-chemical Processes. By GILBERT N. LEWIS (*Zeit. physikal. Chem.*, 1901, 38, 205—226).—A thermodynamical paper, largely unsuitable for abstraction. The tendency of each particle of a phase to pass over into another phase (see this vol., ii, 10) is termed 'fugacity,' and the scope and bearing of the latter are fully dealt with. On the basis of thermodynamical laws, a general equation is deduced, involving the 'fugacity,' and embracing every possible change of state of a simple substance. J. C. P.

A Property of Monatomic Gases. By DANIEL BERTHELOT (*J. Physique*, 1901, 10, 611—614).—It follows directly from van der Waals' equation that at the critical temperature $8/3P_cV_c = RT_c$. The equation, however, assumes incompressibility of the molecules themselves, and the ratio RT_c/P_cV_c is in all cases hitherto examined greater than $8/3$, and higher for more complex than for simpler molecules. In the case of argon, a monatomic gas, $P_c = 52.8$ atmospheres, $T_c = 155.6^\circ$ (absolute), and although the critical density is not known, it may be calculated approximately, the value being probably between 0.434 and 0.448. From these values, the ratio $RT_c/P_cV_c = 2.62$ to 2.71, a result in good accord with the theoretical value. L. M. J.

Reciprocal Salt Pairs. III. Melting Points of Reciprocal Salt Pairs; the Preparation for Analysis and the Synthesis of Minerals by Double Decomposition. By WILHELM MEYERHOFFER (*Zeit. physikal. Chem.*, 1901, 38, 307—325. Compare Abstr., 1896, ii, 414; 1899, ii, 410; 1900, ii, 198).—In the discussion of the melting point of reciprocal salt pairs, it is shown that both the stable and the metastable pairs can give either three congruent, or one congruent and one incongruent product, according as the salt pair remains unchanged, or deposits a third salt on fusion. If on melting no metastable condition occurs, the stable salt pair can be distinguished from the metastable pair by varying the proportions; in the case of congruent melting, the stable pair has only one melting point, but the metastable pair has three, according to the proportions, whilst in the case of incongruent melting, the stable pair has again only one melting point, but the metastable pair has two. These relationships are illustrated by the salt pair $\text{NaBr} + \text{KCl}$. A molecular mixture of these melts at a certain temperature (T_0) until the sodium bromide is completely fused; the temperature then rises until the saturation point of potassium chloride in fused sodium bromide is reached. Addition of sodium bromide or potassium chloride does not change the melting point, but causes more distinct or less distinct fusion at the temperature T_0 on account of the larger or smaller proportion of fused substance

to that which remains solid. On addition of one of the other salts, sodium chloride or potassium bromide, the melting point is lowered to T_1 or T_2 . A mixture of sodium chloride and potassium bromide in molecular proportion likewise melts at T_0 , because it is completely transformed into a mixture of sodium bromide and potassium chloride. On addition of sodium chloride or potassium bromide, the melting point is lowered to T_1 or T_2 , and addition of either of the other salts, sodium bromide or potassium chloride, causes no change of melting point. The stable salt pair ($\text{NaBr} + \text{KCl}$) has only one melting point (T_0), but the metastable pair ($\text{NaCl} + \text{KBr}$) has three (T_0, T_1, T_2), according to the proportion of each constituent.

Experiments on the fusion of mixtures of barium carbonate and potassium sulphate, and of barium sulphate and potassium carbonate prove that the former is the stable salt pair. The fused mixture deposits very little, if any, barium sulphate on cooling, but on treatment with water, reaction may take place so as to produce this. The amount of barium found in the residue as carbonate amounted to 90 to 95 per cent., no matter whether barium carbonate was fused with potassium sulphate, or barium sulphate with potassium carbonate, and the method was such as to give always too low results for this. The rate of cooling appears to have a slight influence on the amount of carbonate found.

The preparation of minerals for analysis, and the pyrochemical synthesis of minerals by double decomposition, are simply cases of converting a metastable salt pair into a stable pair. J. McC.

Observations on the Boiling Points of some Organic Liquids. By G. G. LONGINESCU (*Ann. Sci. Univ. Jassy*, 1901, 1, 359—371).—The additive property of the boiling point may be considered as due to the number of atoms in the molecule, and to the number of molecules in unit volume. Its constitutive character depends on the nature of the elements in the compound, the more or less complex arrangement of the molecules, and the arrangement of the atoms in the molecule. The author compares the ratio of the boiling points (absolute scale) of organic liquids with the ratio of the molecular weights and that of the densities. For compounds of carbon, hydrogen, and oxygen having the same number of atoms in the molecule, $T/T' = M/M'$ (T and M being the boiling point and molecular weight of the compounds). In these cases, therefore, the boiling point is proportional to the molecular weight.

Comparing the ratios for similar substances containing different numbers of atoms in the molecule, it is found that $T/T' = M/M' \cdot \sqrt{n/n'}$ (n and n' being the number of atoms in the molecule).

A comparison of compounds, containing, besides carbon, hydrogen, and oxygen, also nitrogen, sulphur, silicon, boron, bismuth, or mercury, proves that the same regularities obtain.

Association of molecules may give rise to an abnormally high boiling point, for the liquid may be regarded as being composed of simple molecules in which double molecules are dissolved, and in this way the boiling point is raised. On this ground, the irregularities in the first terms of a series of alcohols, ethers, or esters can be accounted for. J. McC.

Vapour Tensions of Mixtures of Ether and Chloroform. By PH. KOHNSTAMM and B. M. VAN DALFSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 156—159). Compare Kohnstamm, this vol., ii, 145).—The vapour pressure curve of mixtures of ether and chloroform at 33.25° has a minimum close to the border, and seems to have also a point of inflexion. The results are at variance either with van der Waals' theory, or with the Galitzin-Berthelot rule.

J. C. P.

Vapour Pressures of Ternary Mixtures. By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1901, 38, 227—255).—A continuation of the author's previous work (this vol., ii, 146, 224, 305, 372, 436). In the present paper, the case of a ternary mixture with three possible liquid phases is treated theoretically; the system water—ether—succinonitrile fulfils these conditions, and has already been experimentally investigated by the author (*Abstr.*, 1898, ii, 329).

The influence of foreign substances on the vapour pressure or boiling point of binary mixtures (homogeneous and non-homogeneous) is also discussed (compare this vol., ii, 445). The addition of a third substance may raise or lower the boiling point of a homogeneous binary mixture according to the nature of its components; where, however, the mixture has itself a maximum or minimum boiling point, it behaves like a pure solvent.

J. C. P.

Calculation of the Heat of Volatilisation and Heat of Fusion of some Elements. By ROBERT DE FORCRAND (*Compt. rend.*, 1901, 133, 513—515).—From the general formula already referred to (this vol., ii, 594), the heat of volatilisation of certain elements can be calculated, although it has not yet been directly determined. The latent heat of vaporisation of phosphorus, for example, is 4200 cal. It follows that $P \text{ (gas)} + 3H \text{ (gas)} = PH_3 \text{ (gas)}$ develops +9100 cal., and $2P \text{ (gas)} + 5O \text{ (gas)} = P_2O_5$ develops 372200 cal.

In the case of arsenic, the molecular weight is not so definitely known as in the case of phosphorus, but assuming the molecule at its boiling point to be As_4 , the heat of vaporisation is 5138 cal., and hence $As \text{ (gas)} + 3H \text{ (gas)} = AsH_3 \text{ (gas)}$ develops -39060 cal.

In the case of selenium, assuming that the molecule is Se_2 at its boiling point, the latent heat of volatilisation is 14595 cal. $Se \text{ (gas)} + 2H \text{ (gas)} = SeH_2 \text{ (gas)}$ develops -4805 cal., but if the constitution of the selenium molecule changes with the temperature, the heat of formation of the hydride may become positive.

C. H. B.

Thermochemistry of very Dilute Solutions. By H. von STEINWEHR (*Zeit. physikal. Chem.*, 1901, 38, 185—199).—The most delicate thermometers being useless in calorimetric work where the temperature change is of the order 0.01°, the author has worked out a differential method, involving the employment of thermo-couples. The reaction to be studied takes place in one of two glass vessels, isolated from each other, and protected from external variations of temperature. If the heat effect of the reaction is positive, the temperature of the solution in the other calorimeter is simultaneously raised by means of a glow lamp; if the heat effect is negative, the

glow lamp is put in the same vessel, so that there is practically no change of temperature. The glow lamp has been successfully employed as a means of supplying a definite quantity of energy. The method avoids disturbing temperature changes before and after the reaction, and permits the determination of temperature differences amounting to a few ten-thousandths of a degree and upwards. The heats of dilution of sulphuric and hydrochloric acids have been determined, also the heats of neutralisation of hydrochloric acid with sodium and barium hydroxides, the numbers obtained for the latter agreeing well with Thomsen's values. In particular, the author has determined the heats of dissociation for a number of electrolytes by adding a small quantity of a strong acid (hydrochloric) to a dilute solution of the sodium salt of a weak acid. This produces a certain quantity of undissociated weak acid, and the heat change, less the heat of dilution of the strong acid, is a measure of the heat of dissociation of the weak acid. Amongst others, the following heats of dissociation are recorded:—formic acid, -366 cal. at 13.1° ; acetic acid, -304 cal. at 17.5° ; dichloroacetic acid, $+1713$ cal. at 17.2° ; butyric acid, $+277$ cal. at 15.5° ; benzoic acid, -495 cal. at 13.5° ; salicylic acid, -1317 cal. at 13.45° ; hydrocyanic acid, -11100 cal. at 15° ; phenol, -5940 cal. at 14.6° ; hydrofluoric acid, $+3006$ cal. at 19.5° ; tartaric acid (first stage of dissociation), -863 cal. at 15° . Many of the values differ considerably from those given by Arrhenius. The variation of the heat of dissociation with temperature for butyric, benzoic, and salicylic acids as found by the author agrees with the results of Arrhenius and of Euler (compare Arrhenius, *Abstr.*, 1889, 1044; 1892, 931; Petersen, *Abstr.*, 1893, ii, 259; Euler, *Abstr.*, 1897, ii, 88). J. C. P.

Relations between Solubility and Heat of Solution. By ADOLFO CAMPETI (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 99—102).—From the relation arrived at by van't Hoff from a study of the influence of temperature on chemical equilibrium, namely, $q = -RT^2 (d \log K / dT)$, T being the absolute temperature, R the constant of the gas equation, K the equilibrium constant of the action considered, and q the amount of heat evolved by a gram-mol. of substance when no external work is done, the author derives the equation: $q = -4.58 (\log K_2 - \log K_1) T_1 T_2 / (T_2 - T_1)$, where K_1 and K_2 are the values of the equilibrium constant at the temperatures T_1 and T_2 . This equation can be applied to determine the quantity of heat evolved or absorbed by the solution of a substance in a solvent, when the concentrations c_1 and c_2 of the saturated solutions at T_1 and T_2 are known, K_1 and K_2 being then represented by c_1 and c_2 respectively. For this relation to hold, it is necessary that the dissolved substances shall not be dissociated, and the author has applied it to carbamide and to mannitol. The following table gives for carbamide the number of grams p which dissolve in 100 grams of water at t° , d being the density of the solution.

| t . | p . | d . |
|-------|--------|-------|
| 9.85° | 84.97 | 1.132 |
| 14.92 | 96.46 | 1.141 |
| 19.92 | 108.17 | 1.151 |

For the heat of solution, the mean values obtained were: $q = -3645$ cal. between 10° and 15° , and -3566 cal. between 15° and 20° , the corresponding numbers calculated from the formula being -2363 cal. between 10° and 15° , and -1752 cal. between 15° and 20° . If, instead of the true concentration, c be taken to represent the number of grams of substance present to every 100 of water in a saturated solution, the numbers agree better, being -4046 and -3833 cal. respectively.

In the case of mannitol, the numbers obtained were:

| $t.$ | $p.$ | $d.$ |
|--------|-------|-------|
| 10.00° | 13.94 | 1.044 |
| 15.01 | 16.18 | 1.050 |
| 20.02 | 18.98 | 1.057 |

$q = -5004$ cal. between 10° and 15° , and -5012 cal. between 15° and 20° , the calculated values being -4380 cal. and -4731 cal.; whilst if c represent grams of substance per 100 of water, $q = -4788$ cal. and -5342 cal. for the ranges of temperature $10-15^\circ$ and $15-20^\circ$ respectively.

Remembering that a small error in the ratio c_1/c_2 makes a relatively great difference in the value of q , it is seen that from the formula given the heat of solution can be calculated with fair approximation from the variation of solubility, c being taken to represent the number of grams of substance added to a constant weight of the solvent to give a saturated solution.

T. H. P.

Temperature Coefficient of the Susceptibility of some Salt Solutions of the Iron Group, particularly of Ferric Chloride. By HUGO MOSLER (*Ann. Phys.*, 1901, [iv], 6, 84—95).—The temperature coefficient of susceptibility has been determined by Wiedemann's method for solutions of ferric chloride and nitrate, cobalt nitrate, and manganese and nickel sulphates. In the case of ferric chloride there is a maximum value of the coefficient, corresponding with the concentration 33 per cent. The results in general agree well with those of Jäger and Meyer (*Sitzungsber. K. Akad. Wiss. Wien*, 1897, 106, 594).

J. C. P.

Remarkable Phenomena in the Neighbourhood of the Critical Point of partially Miscible Liquids. By JACOB FRIEDLANDER (*Zeit. physikal. Chem.*, 1901, 38, 385—440).—In the case of two partially miscible liquids, it is observed that just before complete homogeneity an opalescence is seen, and this phenomenon, together with the physical properties of the liquid solutions near the critical point, was investigated, chiefly in the case of isobutyric acid and water. The temperatures of complete miscibility for mixtures varying to the extent of about 9 per cent. on each side of the critical mixture were determined to about 0.01° . It was found that mixtures in the neighbourhood of the critical point exhibited no alteration of volume, conductivity, or internal friction on standing for 24 hours, they are hence in a stable condition, which is determined solely by temperature and composition. The opalescence also does not exhibit a time alteration, and in this respect differs from that produced in water by the addition of a solution of resin, when the opalescence decreases on standing. The internal friction was determined for various solutions at different

temperatures, and it was found that the temperature coefficient of the friction attained a maximum in the case of the liquid of the critical composition, this maximum being most marked near the critical temperature. Similar results were also obtained for other liquid mixtures, namely, phenol-water, and benzene-water-acetic acid. Analogous results were also found for the opalescence, which increases greatly as the liquid approaches the critical mixture. The coefficient of expansion, the conductivity, and the refractive index do not, however, show any marked variation when the critical state is approached, the refractive index being in good accord with that calculated additively. The author considers the cause of the opalescence to be, most probably, the separation of the liquid into minute drops, which differ, however, from ordinary suspensions, inasmuch as being of almost similar composition there is no distinct surface of separation. L. M. J.

The Equation of Condition and the Theory of Cyclic Motion. By JOHANNES D. VAN DER WAALS (*Zeit. physikal. Chem.*, 1901, 38, 257—288).—A mathematical paper, in which it is shown that a and b in the equation $(p + a/v^2)(v - b) = RT$, are constant for varying temperature and pressure only for monatomic gases. From Helmholtz's theory of cyclic motion, the variation of a and b with temperature and pressure for di- and poly-atomic molecules is deduced, and it is proved that the value of b varies with the pressure. The ratio of the specific heats, C_p/C_v , for diatomic molecules is 1.4, for triatomic molecules 1.2857. J. McC.

Thermal Properties of *iso*Pentane compared with those of Normal Pentane. By J. ROSE-INNES and SYDNEY YOUNG (*Phil. Mag.*, 1901, [vi], 2, 208—210. Compare Abstr., 1899, ii, 587).—If $RT - p_i v$ be 'the departure from Boyle's law' for *isopentane*, and $RT - p_n v$ that for normal pentane at the same temperature and volume, it is found that $RT - p_i v = \lambda(RT - p_n v)$, where λ is a constant. Thus, when $\lambda = 0.9463$ (according to the experimental data near the critical point of normal pentane), and when the values of $p_i v$, as calculated for the isothermals 280°, 240°, 200°, 160°, and 120°, from the data for normal pentane, are plotted against $v^{-\frac{1}{2}}$, the resulting curves agree very well with those obtained directly from experiment. J. C. P.

Isobaric Aqueous Solutions. By J. A. GROSHANS (*Zeit. physikal. Chem.*, 1901, 38, 163—174).—An application of the author's theory of 'density numbers' (Densitätszahlen). Isobaric solutions are obtained by taking two salts of the same 'density number,' and dissolving a molecule of each in equal quantities of water. According to the author, such solutions are of equal density. J. C. P.

Specific Volume of Liquids at Infinite Pressure. By STEFANO PAGLIANI (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 69—74).—From the equation of van der Waals, reduced to its simplest form for the case of a rarefied gas, Tumlirz (*Sitzungsber. K. Akad. Wiss. Wien*, 1900, 109, 837—848) deduced the relations:

$$(1) -1/v \cdot (\delta v / \delta p) T = 12.225m(v - a)^2 / Tv,$$

and

$$(2) (v_1 - v_n) = 12.225m(p_n - p_1)(v_1 - a) / T \cdot (v_n - a),$$

v being the volume in c.c. of a kilogram of the gas, m its molecular weight, p the pressure in atmospheres, v_1, v_n the specific volumes corresponding with the pressures p_1 and p_n , and a the constant of van der Waals' equation. Expression (1) gives the coefficient of compressibility of the liquid, whilst the constant a is obtained from (2). The values calculated from these equations for the compressibilities of a number of liquids do not show good agreement with the values experimentally obtained by several observers, and the author considers the deviations to be due to the fact that a varies with the temperature. The author has calculated the values of a at various temperatures for a number of liquids, and finds that in general it tends to increase as the temperature is raised, except in the case of ethyl ether, where a decrease occurs; with this ether, too, the ratio of the coefficient of compressibility at 100° to that at 0° is more than 3, whilst with the other liquids examined it is always below 2. In the following table, the values of a are given, together with n , the number of atoms in the molecule, and ma the product of mol. weight with the constant a :

| | n . | a . | ma . |
|--------------------------|-------|------------|----------|
| Mercury | 1 | 0.00006798 | 0.013595 |
| Water | 3 | 0.00074573 | 0.013423 |
| Carbon disulphide | 3 | 0.00064052 | 0.048680 |
| Ethyl alcohol | 9 | 0.0009970 | 0.045862 |
| Propyl „ | 12 | 0.0010199 | 0.061194 |
| <i>iso</i> Butyl „ | 15 | 0.0010429 | 0.077175 |
| Amyl „ | 18 | 0.0010517 | 0.092550 |
| Ethyl ether | 15 | 0.0011025 | 0.081590 |
| Benzene | 12 | 0.0009593 | 0.074825 |
| Toluene | 15 | 0.0009865 | 0.090758 |
| Xylene | 18 | 0.0010061 | 0.106647 |
| Cymene | 24 | 0.0010240 | 0.137216 |

From these numbers, it is seen that, in general, the minimum specific volume a , assumed by a liquid under infinitely great pressure, increases with the complexity of the molecule. Further, the values of the product ma which are proportional to the molecular volumes, and hence also the values of $\sqrt[3]{ma}$, proportional to the diameters of the molecules, stand in relation with the molecular complexity.

T. H. P.

Relationship of Viscosity of Liquids to Temperature and Chemical Constitution. By ALEXIUS BATSHINSKI (*Chem. Centr.*, 1901, ii, 450—451; from *Bull. Soc. Imp. Naturalistes Moscou*, 1901, 1—101).—The relationship of viscosity to temperature has been investigated for a large number of liquids. Bromine, nitric oxide, 10 aliphatic hydrocarbons, and 6 ethers behaved in accordance with the general law that the viscosity is inversely proportional to the cube of the absolute temperature. Of 30 halogen derivatives, 6 nitro derivatives, 5 sulphur compounds, and 10 aldehydes and ketones, only 20, 1, 3, and 5 of each class respectively gave the calculated results. Abnormal data were also obtained in the case of anhydrides, acids, and alcohols, and of water below its boiling point. Thirteen aromatic compounds were

examined, but only 5 found to agree approximately with the law. Some esters behaved normally at the ordinary, but others only at a higher, temperature; 38 were examined. E. W. W.

Invisible Liquid Layers and Surface Tension of Liquid Precipitates in the case of Precipitated Membranes, Cells, Colloids, and Jellies. By GEORG QUINCKE (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 858—874).—A detailed record of the phenomena observed when precipitates such as copper ferrocyanide and colloids such as silicic acid or ferric hydroxide separate from an aqueous solution. These phenomena are discussed especially in their relation to the surface tension between the two phases. J. C. P.

Experimental Determination of the Surface Tension of Liquid Air. By LEO GRUNMACH (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 914—918).—By a method previously described (*Ann. Phys.*, 1900, [iv], 3, 660), the surface tension of samples of liquid air containing from 49.9 to 76.7 per cent. of oxygen is found to lie between 11.61 and 12.63 dyne/cm. [For the relative surface tensions of liquid hydrogen, liquid air, and water, compare Dewar, this vol., ii, 597.] J. C. P.

Diffusion of Hydrogen through Palladium. By ADOLF WINKELMANN (*Ann. Phys.*, 1901, [iv], 6, 104—115).—A palladium tube containing hydrogen and raised to a high temperature was connected with a manometer, and the process of diffusion followed by observing the fall of pressure. The quantity of gas which diffuses through the palladium does not diminish proportionally to the pressure. On the supposition (1) that the hydrogen dissociates, (2) that the quantity of gas diffusing is proportional to the pressure of the dissociated molecules, an expression is obtained which gives fairly accurately the relation between the pressure in the apparatus and the quantity of gas diffusing. It is therefore probable that the atoms of hydrogen, not the molecules, pass through palladium at high temperatures (compare Hoitsema, *Abstr.*, 1895, ii, 388). J. C. P.

The use of Reed Tubes for Dialysis. By P. PHILIPPSON (*Beitr. chem. Physiol. Path.*, 1901, 1, 80—82).—Certain tubular membranes of the reed *Phragmites communis* have been recommended for the filtration of bacterial cultures. They are composed of nearly pure cellulose, and lend themselves very well for the separation of colloids and crystalloids, especially when dealing with small quantities of material. Dialysis is stated to occur more rapidly than with parchment paper. W. D. H.

Chemical Equilibria. By OCTAVE BOUDOUARD (*Ann. Chim. Phys.*, 1901, [vii], 24, 5—85).—A *résumé* of earlier papers (compare *Abstr.*, 1899, ii, 287, 365, 417, 595, 596; 1900, ii, 199; this vol., ii, 383) containing a full discussion of the reversible action $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$ and its bearing on certain metallurgical processes. The presence of finely divided solids (amorphous carbon, pumice impregnated with metallic oxides, &c.) increases the velocity of the direct reaction without modi-

fixing the proportions of the gaseous reagents in the final system when equilibrium is attained. G. T. M.

Simultaneous Action of Hydrochloric Acid on Sucrose and Methyl Acetate. By VICTOR HENRI and LARGUIER DES BANCELS (*Compt. rend. Soc. Biol.*, 1901, 53, 784—786).—The velocities of the inversion of sucrose and of the hydrolysis of methyl acetate by hydrochloric acid were determined (1) when proceeding independently, (2) when proceeding simultaneously in the same solution. $N/5$ hydrochloric acid was used, the temperature was 29° , and the velocities were determined by the polarimeter and measurement of the acidity. The results showed (1) that the velocity of inversion of the sucrose was not affected by the presence of the methyl acetate; (2) the velocity of decomposition of the methyl acetate was slightly greater when sucrose was present. L. M. J.

[NOTE.—These results are not in accord with those of Coppadoro (this vol., ii, 544), who found the velocity of inversion of sucrose to be diminished by the presence of methyl acetate.—L.M.J.]

Polymolecular Chemical Transformations. By A. SCHÜKAREFF (*Zeit. physikal. Chem.*, 1901, 38, 353—368).—The speed of the reaction between a ferric salt (chromic acid, or nitrous acid) and an iodide was determined by ascertaining the time which elapsed between mixing these along with a known quantity of thiosulphate to which starch had been added, and the point when the mixture suddenly became blue. From determinations at different concentrations, the number of molecules which take part in the reaction could be calculated. The reaction between ferric salts and metallic iodides is unimolecular for the iron salt and bimolecular for the iodide. The number obtained for ferric chloride is 1.11, for sodium, potassium, calcium, and strontium iodides it is 1.7—1.8. For ferric sulphate, the number is always less than 1 (0.6, 0.8), a result which is possibly due to progressive hydrolysis of the salt. For calcium, strontium, and zinc iodides, the number is 1.7 when the reaction is with ferric chloride, and 2 when it is with ferric sulphate.

In the interaction of chromic acid and iodides, the acid takes part with one molecule. Strontium and calcium iodides act unimolecularly; for sodium iodide, the number is 1.2—1.3.

The reaction between nitrous acid and metallic iodides is polymolecular. The same number (1.6) of sodium iodide and calcium iodide molecules take part in the reaction.

The author believes that the results can be explained by assuming that the iodides are completely dissociated, and the reaction consists of the de-ionisation of the iodine ions. J. McC.

Theory of Solutions. By WALTHER NERNST (*Zeit. physikal. Chem.*, 1901, 38, 487—500).—A résumé of previously published mathematical deductions regarding solutions. An expression for the vapour pressure is first obtained, from which the values for the cryoscopic depression, solubility, electromotive force, and heat of dilution are obtained. A brief reply to Arrhenius (this vol., ii, 144) is added, in which it is pointed out that although he takes exception to the

assumption of the validity of the gaseous laws in solution, yet he himself tacitly makes the same assumption by the calculation of dissociation from the cryoscopic depressions.

L. M. J.

Physical Properties of Albuminous Micelles. By SWIGEL POSTERNAK (*Ann. Inst. Pasteur*, 1901, 15, 570—592).—A continuation of previous papers (this vol., ii, 231 and 544). The phenomena of the coagulation and the whole question of physical properties of proteids are discussed at length.

R. H. P.

Short Methods of Chemical Calculation. By JOSEPH W. RICHARDS (*Chem. Centr.*, 1901, ii, 724—725; from *J. Franklin Inst.*, 1901, 152, 109—112).—The volume of gas formed in any reaction may be calculated by expressing the relative weights of the substances taking part in kilograms, and assuming each molecule of gas liberated to occupy 22.22 cb.m. The weight of carbon, hydrogen, or oxygen contained in 1 cb.m. of any gas is equal to 0.54, 0.045 and 0.72 kilogram respectively, for each atom of the given element present in the molecule.

E. W. W.

A New Laboratory Barometer with Automatic Zero Adjustment. By BENEDIKT WORINGER (*Zeit. physikal. Chem.*, 1901, 38, 326—330).—The level of the mercury in the reservoir of the barometer is kept constant by inserting into the side of the containing vessel a tube of 1 to 2 mm. bore, bent down so that the point just touches the surface of the mercury. This tube is connected with a lower reservoir, from which mercury can be blown up into the higher one. On releasing the pressure, the mercury siphons back until, by the sinking of the level in the upper reservoir, the thread is broken. It is claimed that by this arrangement the level is adjusted to the same position by every operation to within 0.02 mm. A form of vernier for barometers and manometers is also described.

J. McC.

Inorganic Chemistry.

The Two Iodine Monochlorides. By GIUSEPPE ODDO (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 54—58; *Gazzetta*, 1901, 31, ii, 146—151).—In order to determine the nature of the isomerism of the two iodine monochlorides, the author has studied their behaviour in freezing phosphorus oxychloride. The α -modification, which is obtained by the interaction of the calculated quantities of chlorine and iodine, or by distilling four parts of potassium chlorate with one part of iodine, and which crystallises, after melting, at 27.165° , gives a molecular weight corresponding with the formula ICl . Using this monochloride as solvent, with iodine as solute, the molecular freezing point depressions approach the theoretical value as the concentration

increases, whilst with solutions of tetrachloromethane the reverse is the case. All attempts to isolate the β -modification of iodine monochloride described by Stortenbeker (*Abstr.*, 1889, 102), who gave the melting point as 13.9° , were unsuccessful. In one experiment, the thermometer stood at 13.92° during the crystallisation of the product, but suddenly rose to 27.2° . This rapid transformation of the β - into the α -form makes it impossible to examine the cryoscopic behaviour of its solution. Since, however, the β -modification has a lower melting point than the α -form, its molecule must almost certainly have the simple formula.

T. H. P.

Iodine Trichloride. By GIUSEPPE ODDO (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 116—121, and *Gazzetta*, 1901, 31, ii, 151—158).—In freezing phosphorus oxychloride, iodine trichloride gives the molecular weight 134.21—173.42, the calculated value being 233.2. The trichloride is hence dissociated into two parts, which the author considers to be the positive ion, ICl_2 , and the negative ion, Cl . In water, the molecular weight given by the cryoscopic method is 42.00—46.2.

T. H. P.

Active Oxygen obtained by Electrolysis. C. F. BOEHRINGER & SONS (D.R.-P. 117129).—The addition of a manganous salt to the dilute aqueous solution of an oxy-acid (for example, sulphuric acid) contained in the anode cell results in the formation of permanganic acid; this product readily oxidises substances introduced into the cell, and is reconverted into manganous salt. In this way, a small quantity of a manganese compound reacts catalytically in producing an indefinite amount of active oxygen. The agent readily oxidises sulphurous acid, and sulphuric acid having a sp. gr. 1.58 can be obtained in the electrolytic cell. A solution of manganous chloride, on electrolysis, readily yields chlorine and manganese dioxide.

Nitrotoluene, when placed at the anode of an electrolytic cell containing manganous sulphate dissolved in a mixture of dilute acetic and sulphuric acids, is readily oxidised to *p*-nitrobenzoic acid, the temperature being maintained at 80° during the operation. Aniline or quinol, dissolved in dilute sulphuric acid, is readily oxidised to quinone in the presence of manganous sulphate; in either case, the electrolytic cell is surrounded by a freezing mixture.

G. T. M.

Dissociation of the Sulphur Molecule, S_8 . By HEINRICH BILTZ (*Ber.*, 1901, 34, 2490—2495).—The density of sulphur vapour was determined at 440° , under pressures varying from 539.2 to 14 mm.; from 540 to 125 mm., the values agreed with those required for a molecular weight slightly greater than S_7 , but for smaller pressures there was a rapid and continuous diminution of density corresponding with a change from S_7 to S_4 . The curve given illustrating the change shows no break, and the author hence concludes that the dissociation from S_8 to S_2 with increasing temperature above the boiling point is simple, and is not accompanied by the intermediate formation of other aggregates such as S_6 or S_7 .

W. A. D.

Crystalline Form of Telluric Acid. By OTTO BRUNCK (*Ber.*, 1901, 34, 2735—2736).—Telluric acid, prepared by Staudenmaier's

method (Abstr., 1896, ii, 96), crystallises in long, white prisms belonging to the hexagonal system; measurements are given of the two chief angles. T. M. L.

[Sulphur Trioxide and its Dimeric Form.] By GIUSEPPE ODDO (*Gazzetta*, 1901, 31, ii, 158—170).—The author finds that in freezing phosphorus oxychloride solution, the liquid form of sulphur trioxide melting at 14.8° has the normal molecular weight whilst the other form, which decomposes without melting, has a molecular weight corresponding with that required for the formula S_2O_6 ; the latter compound is termed 'disulphuric anhydride.' Under the ordinary pressure, disulphuric anhydride begins to give off sulphur trioxide at about 50° . Sulphur trioxide is much more active chemically than the dimeric form. Thus, a drop of it immediately carbonises organic tissues, whilst in animals it produces profound ulceration; on the other hand, disulphuric anhydride is without action on such materials, provided it does not remain long enough to become hydrated. Sulphur trioxide reacts energetically with powdered camphor, but the dimeric form is without action for some time, after which vigorous action sets in, dissociation previously taking place. Sulphur trioxide does not react with any of the metals, not even with sodium or potassium, or with powdered metallic oxides; sodium oxide is acted on slightly, but the action is stopped by adding excess of the anhydride. Pieces of disulphuric anhydride remain unaltered for some days when placed at the bottom of an open test-tube, but sulphur trioxide, under the same conditions, is rapidly changed into its polymeric form. T. H. P.

Borimide. By ALFRED STOCK and MARTIN BLIX (*Ber.*, 1901, 34, 3039—3047. Compare this vol., ii, 237).—The compound, $B_2S_3 \cdot BBr_3$, formed as a bye-product in the preparation of metathio-boric acid, or more readily by dissolving this acid in excess of boron bromide, is obtained in colourless crystals melting somewhat above 100° , and at higher temperatures decomposing into boron bromide and sulphide. The corresponding chloride, $B_2S_3 \cdot BCl_3$, is also obtained in colourless crystals. The compound $B_2S_3 \cdot 6NH_3$ is obtained in ill-defined, yellow crystals by dissolving the thio-acid in liquid ammonia and evaporating off the excess of this reagent at the ordinary summer temperature.

Borimide, $B_2(NH)_3$, results from the decomposition of the preceding compound at 115 — 120° , in accordance with the equation $B_2S_3 \cdot 6NH_3 = 3NH_4SH + B_2(NH)_3$; the product retains traces of sulphur, and the operation is continued for some days in a rapid current of ammonia. The compound is finally obtained as a light, white powder, decomposed by water with development of heat into boric acid and ammonia. At 125 — 130° , borimide begins to evolve ammonia, and at higher temperatures it decomposes quantitatively into boron nitride and ammonia. Borimide is insoluble in all the indifferent solvents, but when shaken up with liquid ammonia it greatly increases in volume, yielding a gelatinous substance resembling aluminium hydroxide.

The **hydrochloride**, $B_2(NH)_3 \cdot 3HCl$, produced by shaking up the imide with liquid hydrogen chloride, is a white powder insoluble in all the ordinary organic solvents and decomposed by water; it is decomposed by heat into boron nitride, ammonium chloride, and hydrogen chloride.

The boron nitride, produced by the decomposition of borimide or its hydrochloride, is more reactive than the ordinary form of this compound; it is rapidly decomposed by hot water or by dilute sodium hydroxide and ammonia solutions. When ignited in the blowpipe, this reactive modification is converted into the ordinary variety, the change being probably due to polymerisation.

Although borimide is insoluble in liquid ammonia, it rapidly dissolves in this solvent on the addition of sulphur, yielding a dark blue solution. The coloured product is more stable than that obtained from sulphammonium and sulphur (compare Moissan, this vol., ii, 234), and is obtained after evaporating off the solvent as a deep blue, amorphous substance stable in dry air, and yielding blue solutions with water or absolute alcohol; it is immediately decomposed by acids with the separation of sulphur, and undergoes a slow decomposition in aqueous solution. This colour reaction is extremely delicate, and serves as a test for traces of free sulphur; a similar coloration was formerly observed on treating nitrogen sulphide containing traces of sulphur with a dilute alcoholic solution of potassium hydroxide; these effects may be due to the formation of analogous products.

G. T. M.

Phenomena of Combustion in Furnaces. By OCTAVE BOUDOUARD (*Bull. Soc. Chim.*, 1901, [iii], 25, 833—840).—The results obtained in the study of the reaction $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$ (Abstr., 1899, ii, 417, 596; this vol., ii, 314, 646) are of importance in connection with the working of gas producers, blast-furnaces, and reverberatory furnaces. In the production of air-gas, it is shown that the temperature should be as near 1000° as is possible, the combustible substance in a finely-divided and porous state, and the velocity of the gas low. The fulfilment of similar conditions is necessary in the lower regions of blast-furnaces, and the height of the furnace and velocity of the gases must be so proportioned as to bring about the reduction of the ore without loss of carbon monoxide and consequent waste of fuel. When the mere fusion of metal is required, complete combustion with the minimum quantity of air is to be aimed at. The combustible should, therefore, present as small a surface as possible, the velocity of the gases should be high, in order to diminish the time of contact of the carbon dioxide with the fuel, and the products of combustion should be quickly cooled by a large charge of metal.

N. L.

Carbon Oxysulphide. By WALTHER HEMPEL (*Zeit. angew. Chem.*, 1901, 14, 865—868. Compare Klason, Abstr., 1887, 1015).—As carbon oxysulphide is readily decomposed in the presence of moisture, it is best purified by liquefaction, and stored in the liquid state. The gas is passed through alkali (1 in 2), concentrated sulphuric acid, a mixture of triethylphosphine, pyridine, and nitrobenzene, and cooled, first by the aid of a freezing mixture of ice and salt to remove less volatile impurities, and then with solid carbon dioxide and ether to condense the oxysulphide. The pure compound has only a faint odour, but acts quickly on the nervous system. It boils at -47.5° under atmospheric pressure; its critical temperature is 105° , and the pressure 63 kilos. per sq. cm. One c.c. of water dissolves 0.8 c.c. of the compound at 13.5° and 756 mm., whereas 1 c.c. of a concentrated solution of cuprous

chloride in hydrochloric acid dissolves only 0.2 c.c. Mixtures of air and carbon oxysulphide are still explosive when they contain 11.9—28.5 per cent. of the gas.

In the analysis of gaseous mixtures containing carbon oxysulphide, hydrogen sulphide, and carbon dioxide, the hydrogen sulphide is first absorbed by acidified copper sulphate solution, the gas is then heated in a platinum capillary tube at 120°, when the oxysulphide is decomposed into sulphur and carbon monoxide; the latter is absorbed with acidified cuprous chloride, and then the carbon dioxide with alkali. J. J. S.

Metasilicic Acid. By VASILE C. BUTZUREANU (*Ann. Sci. Univ. Jassy*, 1901, 1, 319—320).—Precipitated gelatinous silicic acid is dehydrated by 90 per cent. alcohol and a white powder obtained which on ignition loses about 22 per cent. of water. The existence of metasilicic acid, $\text{SiO}(\text{OH})_2$, is thus proved. J. McC.

Purification of Cæsium Material. By HORACE L. WELLS (*Amer. Chem. J.*, 1901, 26, 265—268).—The author finds that the lead tetrachloride method of precipitating cæsium from its solutions (Abstr., 1893, ii, 521), although useful for removing small quantities of the metal, is inconvenient when large quantities are dealt with. He has therefore abandoned this method in favour of a modification of that of Godeffroy, in which the metal is precipitated as cæsium antimony chloride. When a high degree of purity is required, it is best obtained by means of the salt CsCl_2I (Wells and Penfield, Abstr., 1892, 773), from which pure cæsium chloride may be prepared by gentle ignition. E. G.

Cæsium-Tellurium Fluoride. By HORACE L. WELLS and J. M. WILLIS (*Amer. J. Sci.*, 1901, [iv], 12, 190).—The only cæsium-tellurium fluoride which it has been possible to obtain is CsF_2TeF_4 . It is prepared by adding cæsium fluoride to a hydrofluoric acid solution of tellurium fluoride, and crystallises in transparent, colourless needles which are decomposed by water. J. McC.

Acid Nitrates. By HORACE L. WELLS and F. J. METZGER (*Amer. Chem. J.*, 1901, 26, 271—275).—By saturating nitric acid of sp. gr. 1.42 with the normal nitrates of rubidium and cæsium at a gentle heat and cooling the solutions, the salts, $\text{RbNO}_3\cdot\text{HNO}_3$ and $\text{CsNO}_3\cdot\text{HNO}_3$, are readily prepared; by dissolving the normal nitrates in nitric acid of sp. gr. 1.50 and cooling with a freezing mixture, the salts, $\text{RbNO}_3\cdot 2\text{HNO}_3$, $\text{CsNO}_3\cdot 2\text{HNO}_3$, and $\text{TiNO}_3\cdot 2\text{HNO}_3$, are obtained. The salts, $2\text{RbNO}_3\cdot 5\text{HNO}_3$ and $\text{TiNO}_3\cdot 3\text{HNO}_3$, described by Ditte (Abstr., 1880, 153), could not be isolated. The mono-acid salts form large, flat masses of small, colourless, transparent crystals. The di-acid salts, $\text{RbNO}_3\cdot 2\text{HNO}_3$ and $\text{TiNO}_3\cdot 2\text{HNO}_3$, form colourless, transparent needles, whilst $\text{CsNO}_3\cdot 2\text{HNO}_3$ crystallises in large, thin, colourless, transparent plates. The salt $\text{RbNO}_3\cdot\text{HNO}_3$ melts at 62°, $\text{CsNO}_3\cdot\text{HNO}_3$ at 100°, $\text{RbNO}_3\cdot 2\text{HNO}_3$ at 39—46°, and $\text{CsNO}_3\cdot 2\text{HNO}_3$ at 32—36°. All the acid nitrates lose nitric acid more or less rapidly on exposure to the air. E. G.

Double Nitrates. By HORACE L. WELLS, H. P. BEARDSLEY, G. S. JAMIESON, and F. J. METZGER (*Amer. Chem. J.*, 1901, 26, 275—278).—*Cæsium ferric nitrate*, $\text{CsNO}_3 \cdot \text{Fe}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$, forms pale yellow, deliquescent, prismatic crystals and melts at 33—36°.

Cæsium bismuth nitrate, $2\text{CsNO}_3 \cdot \text{Bi}(\text{NO}_3)_3$, crystallises in long, colourless prisms and melts at 102°.

Thallous thallic nitrate, $2\text{TlNO}_3 \cdot \text{Tl}(\text{NO}_3)_3$, separates in large, colourless, transparent, prismatic crystals, and melts at 150°; it is stable in dry air, but blackens when exposed to moisture. E. G.

Cæsium Periodate and Iodate-Periodate. By HORACE L. WELLS (*Amer. Chem. J.*, 1901, 26, 278—281).—*Cæsium periodate*, CsIO_4 , obtained by dissolving the carbonate in concentrated solutions of periodic acid, crystallises in white plates, and dissolves sparingly in cold, but more readily in hot, water.

Cæsium hydrogen iodate-periodate, $\text{HCsIO}_3 \cdot \text{IO}_4 \cdot 2\text{H}_2\text{O}$, crystallises in slender, white prisms from a solution of cæsium periodate in dilute periodic acid, in which the periodate has suffered partial reduction; it may also be prepared by cooling a solution of cæsium iodate and periodate in dilute periodic acid. E. G.

Combination of Haloid Lithium Salts with Ammonia and Amines. By J. BONNEFOI (*Ann. Chim. Phys.*, 1901, [vii], 23, 317—378. Compare Abstr., 1897, ii, 371; 1899, i, 185, and ii, 96; 1900, ii, 130 and 478).—This communication contains a *résumé* of the study of the phenomenon of chemical dissociation as induced by changes of pressure and temperature, and the application of Clapeyron's formula to the verification of experimental results, particularly those obtained in investigating the compounds of metallic halogen salts with ammonia and the amines. The greater portion of the experimental data has already been published, but the following results are described for the first time. The compound $\text{LiCl} \cdot \text{NHMe}_2$, the sole product of the action of dimethylamine on lithium chloride, is a white, bulky substance, the molecular heat of dissolution of which is 9·242 Cal., its heat of formation from the gaseous amine and salt being 13·820 Cal. The heat of dissolution of the gaseous dimethylamine is 14·635 Cal. Trimethylamine, diethylamine, and triethylamine combine with lithium chloride in one proportion only, giving rise to compounds $\text{LiCl} \cdot \text{NMe}_3$, $\text{LiCl} \cdot \text{NHEt}_2$, and $\text{LiCl} \cdot \text{N}(\text{Et})_3$, respectively; the heats of formation of these substances from the amine and the salt are, respectively, 13·774, 10·638, and 10·887 Cal., the heats of dissolution of the products being 7·603, 13·509, and 16·350 Cal. Lithium chloride combines with 1, 2, and 3 mols. of propylamine, butylamine, isobutylamine, amylamine, or hexylamine; it also interacts with aniline, forming $\text{LiCl} \cdot \text{NH}_2\text{Ph}$ and $\text{LiCl} \cdot 2\text{NH}_2\text{Ph}$. G. T. M.

[Non-]Existence of Ammonium. By OTTO RUFF (*Ber.*, 1901, 34, 2604—2607).—If a tube is taken shaped like an inverted Y, platinum electrodes are sealed into the bottom of the two lower limbs, these electrodes surrounded with potassium iodide in small lumps, liquid ammonia is placed over the whole, and a current passed while the apparatus is kept at -70° to -95° by a mixture of liquid air and alcohol, metallic potassium appears to be liberated at the cathode, and, rising into the

upper layers of the liquid ammonia, colours these blue. When ammonium iodide is used, no blue coloration is produced, even when the top limb of the tube is sealed up and the experiment allowed to continue until the tube bursts, which did not happen in one experiment until enough electricity had passed to generate hydrogen gas which must have produced a pressure of 60 atmospheres in the apparatus. It would seem that, even under these favourable circumstances, no metallic ammonium, analogous to metallic potassium, can have been produced. It may be doubted whether such a substance is capable of existence at all. Probably it is better to regard the group NH_4 rather as a compound $\text{H}\cdot\text{NH}_3$ which readily dissociates; it would then be analogous with the compounds of the alkali metals with ammonia, $\text{K}\cdot\text{NH}_3$, $\text{Na}\cdot\text{NH}_3$, $\text{Li}\cdot\text{NH}_3$.
C. F. B.

Basic Energy of Silver Oxide in Solution. By M. G. LEVI (*Gazzetta*, 1901, 31, ii, 1—3).—Contrary to the generally quoted statement of Bineau that 1 part of silver oxide dissolves in 3000 of water, the author finds that at the ordinary temperature this amount of silver oxide requires 15,360 parts of water for its solution. The mean value of the dissociation constant, as determined by the electrical conductivity method for dilutions of 1783 to 14,264, is $100k = 0.0115$; the degree of dissociation for the former dilution is $m = 0.387$, and for the latter, 0.722.
T. H. P.

Action of Hydrogen Peroxide on Silver Oxide. A Reply. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1901, 34, 2769—2774. Compare this vol., ii, 315).—A reply to Berthelot (this vol., ii, 383). The authors have repeated their earlier experiments (*loc. cit.*) on the action of hydrogen peroxide on silver oxide, and have completely confirmed them and the conclusions drawn therefrom. In addition, Berthelot's experiment (*loc. cit.*) has been exactly repeated with every precaution, and it is found that the solid product of the interaction of hydrogen peroxide and silver oxide neither gives off oxygen when treated with sulphuric acid nor contains silver peroxide.

When aqueous sodium carbonate is added to a solution of hydrogen peroxide containing silver nitrate, a white precipitate of silver carbonate is formed, which immediately decomposes with the production of black flakes and a rapid evolution of gas; the latter, from the first, is a mixture of carbon dioxide and oxygen.
K. J. P. O.

Sulphohaloids of Lead. By VICTOR LENHER (*J. Amer. Chem. Soc.*, 1901, 23, 680—682).—When lead sulphoiodide is prepared by adding an aqueous solution of hydrogen sulphide to a solution of lead iodide in strong hydriodic acid, it has the same composition, $\text{PbS}_2\cdot 4\text{PbI}_2$, as that obtained by the method previously described (*Abstr.*, 1896, ii, 523). The sulphochloride, sulphobromide, and sulphoiodide, may all be readily prepared by diluting a solution of lead sulphide in the corresponding strong halogen acid. The sulphofluoride could not be obtained.
E. G.

Volatility of Lead Oxide. By M. STOERMER (*Chem. Zeit.*, 1901, 25, 818).—A series of experiments showing that during the cementation of lead oxide and silica a loss of lead oxide may occur to the

extent of 1·8—16·75 per cent., according to the quantity of oxide present. Once lead silicate is formed, there will be no further loss in lead on melting the mass, unless it should come into contact with reducing gases; a small portion of the oxide will then be reduced to metallic lead, which is still more volatile than the oxide. L. DE K.

Radio-active Lead. By KARL A. HOFMANN and EDUARD STRAUSS (*Ber.*, 1901, 34, 3033—3039. Compare this vol., ii, 19, 159, 385).—Further details are given as to the preparation and properties of radio-active lead salts. Uranium nitrate mother liquors have been used as a source of radio-active lead, and the separation of the latter from arsenic, copper, bismuth (polonium), and iron oxides, and calcium and barium (radium) carbonates is described. Stress is especially laid on the proof that no radium or polonium can be present in the lead salts obtained. The chromate of radio-active lead is not decomposed even on repeated warming with dilute sulphuric acid—a distinction from ordinary lead chromate. Whilst the sulphate alone acts on a photographic plate through aluminium or glass, especially after evaporation with nitric and sulphuric acids or heating for fifteen hours in an open vessel at 450°, all the radio-active lead salts are equally effective in discharging an electroscope. The photographic action of radio-active lead sulphate is greater than that of bismuth (polonium) oxychloride freshly prepared from pitchblende, and is approximately the same as that of the barium (radium) sulphate prepared from the same mineral. A polonium preparation, on the other hand, discharges an electroscope much more rapidly than a radio-active lead preparation. It thus appears that the radiation revealed by the photographic plate is not the same as that responsible for the dissipation of electrical charges.

J. C. P.

The Specific Volume as the Determining Criterion of Chemical Combination in Metal Alloys. By E. MAEY (*Zeit. physikal. Chem.*, 1901, 38, 292—306. Compare Abstr., 1899, ii, 547).—The author has examined the curve representing the change of specific volume with change of composition of a series of twenty-five alloys. In eight cases, it is found that this curve consists of straight lines, intersecting at points which indicate the existence of the compounds SnAg_3 , Au_2Bi_3 , BiPb (or Bi_2Pb_3), FeSb , SnCu_3 , and CuZn_2 . The author points out the utility of this method of examination, and shows that where the curve exhibits a break, there is definite indication of the existence of a compound, but compounds may exist and yet, on account of there being no sudden change of volume, there may be no break in the curve at the corresponding point.

J. McC.

New Determination of the Density of Copper-Tin, Copper-Zinc, and Tin-Zinc Alloys. By E. MAEY (*Zeit. physikal. Chem.*, 1901, 38, 289—291).—The densities of alloys of these metals in various proportions have been determined, and the results do not agree with the previous observations of Riche and Mallet. The following numbers indicate the densities of the alloys examined, poorest and richest in one metal; Copper-tin, 28 per cent. tin, sp. gr. 8·903 at 4°;

80 per cent. tin, sp. gr. 7·735 at 4°: Copper-zinc, 19·8 per cent. zinc, sp. gr. 8·459 at 4°; 94·1 per cent. zinc, sp. gr. 7·311 at 4°: Tin-zinc, 25 per cent. zinc, sp. gr. 7·233 at 4°; 75 per cent. zinc, sp. gr. = 7·110 at 4°.
J. McC.

Combined Action of Carbon Dioxide and Alkali Salts on Cupric Oxide. By OTTO KÜHLING (*Ber.*, 1901, 34, 2849—2852).—Freshly precipitated cupric oxide, suspended in a solution of sodium chloride in one case, and of sodium nitrate in the second, was treated with a stream of carbon dioxide during from two to five days. The bright green amorphous powders obtained had the constitutions represented respectively by the formulæ, $\text{OH} \cdot \text{CuCl} \cdot \text{CuCl}_2 \cdot 5\text{Cu}(\text{OH})_2$, and $\text{OH} \cdot \text{Cu} \cdot \text{O} \cdot \text{CO} \cdot \text{O} \cdot \text{Cu} \cdot \text{OH}$.
R. H. P.

Action of Hydrogen on Mercury Sulphide. By H. PÉLABON (*Bull. Soc. Chim.*, 1901, [iii], 25, 777—785).—Details of work already published (this vol., ii, 545).
N. L.

Crystalline Metallic Compounds of Aluminium. By OTTO BRUNCK (*Ber.*, 1901, 34, 2733—2735).—The alloy Cu_4Al_9 is obtained in the form of long, white, glistening crystals by melting together equal weights of aluminium and copper, and pouring off the mother liquor as soon as crystallisation has begun; it has a sp. gr. 4·118, is not readily soluble in nitric acid, but dissolves easily in aqua regia; hydrochloric acid decomposes it, dissolving the aluminium, and leaving a residue of copper.

The alloy FeAl_3 is obtained in stout, iron-grey, glistening crystals by melting together 1 part of iron and 1 part of aluminium and extracting with 2 per cent. hydrochloric acid; the crystals have a sp. gr. 3·734, become bluish in air, and dissolve readily in strong acids.

The alloy NiAl_3 , prepared by a similar method to the iron compound, forms glistening, feathery crystals resembling nickel in colour, has a sp. gr. 3·681, and dissolves completely in strong acids.

The cobalt alloy, $\text{Co}_3\text{Al}_{13}$, differs in composition and in properties from the nickel compound; the fused mass consists of parallel lamellæ which, when etched, dissolve to feathery crystals which are coarser in structure and bluer in colour than the nickel compound.

The alloy Mn_2Al_7 forms tin-white, crystal plates and dissolves readily in strong hydrochloric acid.

The alloy $\text{Pt}_3\text{Al}_{10}$ forms stout, bronzy crystals of indistinct structure; hydrochloric acid dissolves out all the aluminium.
T. M. L.

Gradations in the Properties of Alums. By JAMES LOCKE (*Amer. Chem. J.*, 1901, 26, 166—185. Compare Abstr., 1898, ii, 567).—The solubilities at 25° of 19 alums of the formula $\text{M}'\text{M}''(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ were determined, and the results are given in gram-molecules per litre in the following table:

| | K. | NH_4 . | Tl. | Rb. | Cs. |
|----------|-------|-----------------|-------|-------|--------|
| Al | 0·28 | 0·387 | 0·177 | 0·059 | 0·013 |
| V | — | 1·210 | 0·573 | 0·177 | 0·0204 |
| Cr | 0·441 | 0·407 | 0·212 | 0·078 | 0·0151 |
| Fe | — | 1·659 | 0·799 | 0·293 | 0·045 |
| In | — | — | — | — | 0·172 |

An increase in the atomic weight of the trivalent metal produces a steady increase in the solubility of the alum, except in the case of chromium, which shows an abrupt decrease. The influence of the univalent metal is somewhat similar; the solubility decreases as the molecular weight increases in the series K, Rb, Cs, but the ammonium and thallium alums are abnormal, and (with one exception) are intermediate in solubility between the potassium and rubidium alums. The solubilities were also determined at intervals of 5° up to 40° in the case of 6 alums, and it was found that the more soluble alums had, in every case, the larger temperature coefficients.

In the case of 23 alums, the temperature was determined at which the crystals melt in their water of crystallisation. The results are given in the following table, those obtained by other observers being marked with an asterisk :

| | Na. | K. | Tl. | NH ₄ . | Rb. | Cs. |
|----------|-----|-----|-----|-------------------|------|------|
| Al | 63° | 91° | 91° | 95° | 109° | 122° |
| V | 9* | 20* | 48 | 45 | 64 | 82 |
| Cr | — | 89 | 92 | 94 | 107 | 116 |
| Fe | — | 28 | 37 | 40 | 53 | 71 |
| Co | — | — | — | — | 47 | 63 |
| In | — | — | — | 36* | 42 | — |

These figures correspond closely with the results of the solubility determinations, the melting point falling as the solubility increases; in the series Al, V, Fe, Co, the melting point falls as the atomic weight of the trivalent metal increases, whatever the nature of the univalent metal, but here again chromium shows an exceptional behaviour, and the melting points of the chromium alums are abnormally high.

T. M. L.

Indium. By CARL RENZ (*Ber.*, 1901, **34**, 2763—2765).—Indium can be readily estimated by precipitating the hydroxide from hot solutions of indium salts by means of dimethylamine. After filtration, the hydroxide is separated as far as possible from the filter paper, ignited, and weighed as the sesquioxide.

Indium hydroxide behaves as a weak acid and forms indates. *Magnesium indate*, $\text{MgIn}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, prepared by boiling an aqueous solution of magnesium and indium chlorides, is a white, insoluble powder.

Indium molybdate, $\text{In}_2(\text{MoO}_4)_3 \cdot 2\text{H}_2\text{O}$, is formed as a voluminous precipitate when a solution of ammonium molybdate is added to solutions of indium salts, and can be used to separate indium and zinc.

Indium platincyanoide, $\text{In}_2(\text{Pt}[\text{CN}]_4)_3 \cdot 2\text{H}_2\text{O}$ (?), is prepared by boiling solutions of indium sulphate and barium platincyanoide, crystallises in white, hygroscopic leaflets, and in aqueous solution gives a characteristic blue precipitate with mercurous nitrate.

K. J. P. O.

Barium Manganate and Manganite. By GEORG KASSNER and H. KELLER (*Arch. Pharm.*, 1901, **239**, 473—490).—(1) The preparation of potassium manganate by evaporating a solution of potassium permanganate and hydroxide and heating the residue at 300° in the absence of carbon dioxide, requires an amount of hydroxide equal to

$1\frac{1}{2}$ —2 times that corresponding with the equation $4\text{KMnO}_4 + 4\text{KOH} = 4\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} + \text{O}_2$, in order to prevent the product from decomposing when it is dissolved. (2) The precipitated barium manganate contains, besides barium carbonate and oxides of manganese, some barium permanganate, which forms in the sample as it is kept. (3) Barium manganate does not contain any water of crystallisation or water chemically united. (4) Barium manganite is better formed by using hydrogen peroxide instead of potassium ferrocyanide to reduce the manganate, as the product is then free from iron, and decomposes less readily into barium oxide (or hydroxide) and manganese dioxide when it is washed. (5) Barium manganite appears to contain water of crystallisation corresponding with the formula $\text{BaMnO}_3 \cdot \text{H}_2\text{O}$. It contains, also, barium carbonate, oxides of manganese, and a residue insoluble in acids (barium silicate). C. F. B.

Preparation of [Potassium] Permanganate by means of Ozone. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 118232).—Potassium manganate in a strong alkaline solution is quantitatively converted into permanganate by the action of ozonised air at 40° in accordance with the equation $2\text{K}_2\text{MnO}_4 + \text{O} + \text{H}_2\text{O} = 2\text{KMnO}_4 + 2\text{KOH}$. The potassium permanganate crystallises out, and the potassium hydroxide is readily obtained on evaporation and employed in fusing further quantities of manganese dioxide. G. T. M.

Peroxides of Iron and the Catalytic Action of Iron Salts. By WILHELM MANCHOT and O. WILHELMS (*Ber.*, 1901, **34**, 2479—2490).—In the liberation of iodine from potassium iodide by hydrogen peroxide in presence of a ferrous salt, the iron does not act catalytically, but is itself oxidised; for every ferrous atom present, 2 mols. of hydrogen peroxide are necessary and 2 atoms of iodine are liberated. Taking into account the oxygen used for oxidising the ferrous iron to ferric, the iodine liberated corresponds with the formation of a peroxide, Fe_2O_5 , or a periodide, FeI_5 .

On adding $\frac{1}{2}$ mol. of hydrogen peroxide to a solution of ferrous sulphate (1 mol.), the whole of the latter is rapidly oxidised to ferric sulphate, but on adding the ferrous salt (1 mol.) to the peroxide (0.5—1.4 mols.), both of these are found existing together, especially at 0° , in smaller or greater amount at the end of the operation (contrast Brode, this vol., ii, 443). Varying quantities of oxygen are evolved, and the mixtures give rather variable numbers on titrating back with permanganate. Using 1 mol. of ferrous salt and $1\frac{1}{2}$ mols. of hydrogen peroxide at 0° , the amount of the latter actually used, as found by this process, lies between 1 and $1\frac{1}{2}$ mols., corresponding as before with the formation of Fe_2O_5 .

Ferric salts destroy hydrogen peroxide much more slowly than ferrous salts; it was found that ferrous ammonium sulphate destroyed more hydrogen peroxide in a given time than corresponded with oxidation to the ferric state, whilst under the same conditions ferric ammonium sulphate left a similar solution unaffected.

In acid solution, the interaction of iron salts, hydrogen peroxide, and potassium iodide is complex, the iodine being liberated more slowly; the iron here acts catalytically, and there is no well-defined

end point of the action. The addition of dilute sulphuric acid to a solution of hydrogen peroxide containing sufficient ferric ammonium sulphate to destroy the whole of the peroxide in about 70 hours practically prevented the iron from changing the strength of the solution. Acid also retards the oxidation of ferrous salts by hydrogen peroxide and the addition of oxygen (or hydrogen peroxide) to ferric salts.

W. A. D.

Existence of Trichlorotriaquochromium. By PAUL PFEIFFER (*Ber.*, 1901, 34, 2559—2564. Compare Werner and Gubser, this vol., ii, 453).—When the yellowish-brown double salt,



(pyridinium pentachlorochromate, *Abstr.*, 1900, i, 559), which dissolves readily in water, is stirred rapidly into an aqueous solution of silver nitrate cooled to 0° , and the stirring continued, the silver chloride settles completely and the liquid clears in about 10–15 seconds when the silver present is not equivalent to more than 2·1Cl in the molecule of the double salt; when it is equivalent to more, 25–110 seconds are required. From this, the conclusion is drawn that only 2 of the chlorine atoms are ionised, and that the double salt is to be regarded as a compound of trichlorotriaquochromium with pyridine hydrochloride; it would then have the formula $\text{CrCl}_3(\text{OH}_2)_3 \cdot 2(\text{C}_5\text{NH}_5\text{HCl})$, and would dissociate into $[\text{CrCl}_3(\text{OH}_2)_3] + 2(\text{C}_5\text{NH}_5\text{H})^+$ and 2Cl^- . As the solution is yellowish-green when freshly prepared, this must be the colour of trichlorotriaquochromium, and as the colour of the solution gradually changes to the green colour characteristic of a solution of dichlorotetra-aquochromium chloride, $[\text{CrCl}_2(\text{OH}_2)_4]\text{Cl}$ or $[\text{CrCl}_2(\text{OH}_2)_4]^+$ and Cl^- , a molecular transformation must have taken place, 1 mol. of water being taken up.

It is also possible to suppose that the double salt has the constitution $[\text{CrCl}(\text{C}_5\text{NH}_5\text{HCl})_2(\text{OH}_2)_3]\text{Cl}$, which would dissociate into the ions $[\text{CrCl}(\text{C}_5\text{NH}_5\text{HCl})_2(\text{OH}_2)_3]^{++}$ and 2Cl^- , the more complex of which would then dissociate into $[\text{CrCl}_3(\text{OH}_2)_3]$ (trichlorotriaquochromium) and $2(\text{C}_5\text{NH}_5\text{H})^{++}$.

C. F. B.

Oxides, Sulphides, and Iodides of Molybdenum. By MARCEL GUICHARD (*Ann. Chim. Phys.*, 1901, [vii], 23, 498—574).—A detailed account of work already published (compare *Abstr.*, 1897, ii, 145, 496; 1900, ii, 80, 144, 211, 370, 658, and this vol., ii, 62, 242.)

G. T. M.

Specific Heats of Tungsten and Molybdenum. By EDOUARD DEFACQZ and MARCEL GUICHARD (*Ann. Chim. Phys.*, 1901, [vii], 24, 139—144).—The specific heat of a sample of tungsten containing 99·84 per cent. of the metal is 0·0340, 0·0366, and 0·0375 at 93° , 258° , and 423° respectively. The specific heat at any temperature, T , may be calculated from the equation

$$C_T = 10^{-10}(313903582 \cdot 57 + 516282 \cdot 0216T - 933 \cdot 0108T^2).$$

The specific heat of molybdenum (Mo = 99·78 per cent.) is 0·072, 0·074, and 0·072 at $93 \cdot 25^\circ$, 281° , and 444° respectively; other intermediate values are also given. Regnault found that the specific heats of tungsten between 0° and 100° was 0·03636, whilst that of molybdenum at 100° was 0·07218.

G. T. M.

Uranyl Chloride and Water. By FRANZ MYLIUS and RUDOLF DIETZ (*Ber.*, 1901, 34, 2774—2778).—When a solution of uranic acid in concentrated hydrochloric acid is evaporated in a desiccator over sulphuric acid, a *compound*, $\text{UO}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, separates in yellowish-green, doubly-refracting, hygroscopic prisms, which on heating above 100° give off water, hydrogen chloride, and chlorine. The saturated aqueous solution (containing 76.2 per cent. UO_2Cl_2) is yellowish-green and viscous, and has a sp. gr. 2.74. On evaporation, hydrogen chloride is evolved and from the syrupy residue a *compound*, $\text{H}_4\text{UO}_5\text{Cl} \cdot 2\text{H}_2\text{O}$, separates in flattened needles; this loses its water of crystallisation at 150° and in aqueous solution scarcely reddens blue litmus. From the aqueous solution, silver oxide precipitates the whole of the chlorine, leaving a solution of “colloidal” uranic acid, which, however, immediately and entirely separates if heat is applied. The view is expressed that these substances are compounds of a uranyl hydrate and hydrogen chloride, namely, $\text{H}_4\text{UO}_5 \cdot 2\text{HCl}$ and $\text{H}_4\text{UO}_5 \cdot \text{HCl}$.

K. J. P. O.

Uranium Sulphate. By WILLIAM OECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1901, 23, 349—351).—The densities of aqueous solutions (1—12 per cent.) of the salt $(\text{UO})_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ have been determined and also that of solutions (1—5 per cent.) in sulphuric acid of sp. gr. 1.168. The solubility of the salt in water at the ordinary temperature is about 5 parts in 100. The refractive indices of 8 and 10 per cent. aqueous solutions are 1.365 and 1.371 respectively.

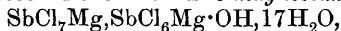
R. H. P.

Double Chlorides of Cæsium and Thorium. By HORACE L. WELLS and J. M. WILLIS (*Amer. J. Sci.*, 1901, [iv], 12, 191—192).—As a rule, double halogen salts of quadrivalent metals belong to the type $2\text{M}^{\text{I}}\text{Cl} \cdot \text{M}^{\text{IV}}\text{Cl}_4$. The double fluorides of zirconium (*Abstr.*, 1897, ii, 558) occur in a variety of types, and it was to be expected that thorium double haloids would also exist. Attempts to prepare a double fluoride of cæsium and thorium gave uncertain results, but two cæsium-thorium chlorides, $3\text{CsCl} \cdot \text{ThCl}_4 \cdot 12\text{H}_2\text{O}$ and $2\text{CsCl} \cdot \text{ThCl}_4 \cdot 11\text{H}_2\text{O}$, have been obtained. The first crystallises from solutions containing about 12 grams of thorium chloride and 30 to 110 grams of cæsium chloride; the second from solutions containing about 65 grams of thorium chloride and 30 to 100 grams of cæsium chloride. The salts are very hygroscopic and on account of the difficulty of drying them the amount of water of crystallisation is uncertain.

J. McC.

Double Salts of Antimony Pentachloride. By RUDOLPH F. WEINLAND and FR. SCHLEGELMILCH (*Ber.*, 1901, 34, 2633—2635).—Antimony pentachloride forms double salts with the chlorides of potassium, ammonium, calcium, and magnesium when a mixture of the two chlorides is dissolved in 15 per cent. hydrochloric acid and the solution cooled. The *potassium* salt, $\text{SbCl}_6\text{K} \cdot \text{SbCl}_5\text{K} \cdot \text{OH}$, forms irregular six-sided, hygroscopic plates. The *ammonium* salt, $\text{SbCl}_6(\text{NH}_4) \cdot \text{SbCl}_5 \cdot \text{NH}_4 \cdot \text{OH}$, crystallises in well-developed six-sided tablets and is not deliquescent.

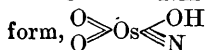
The *calcium* salt, $\text{SbCl}_6 \cdot \text{Ca} \cdot \text{SbCl}_5 \cdot \text{OH} \cdot 9\text{H}_2\text{O}$, crystallises well in long prisms and deliquesces in the air. The *magnesium* salt,



is very hygroscopic and crystallises in long prisms or small plates. This property of antimony pentachloride corresponds with that of stannic chloride, the double salts of which are well known. A. H.

Salt of Quadrivalent Antimony. By HORACE L. WELLS and F. J. METZGER (*Amer. Chem. J.*, 1901, 26, 268—271).—The salt, Cs_2SbCl_6 , first obtained by Setterberg (*Öfver. K. Vetensk. Akad. Förhandl.*, 1882, 23) by boiling a solution of antimony trichloride in strong hydrochloric acid with antimony pentachloride and caesium chloride, crystallises in small, black octahedra, and when rubbed between the ground surfaces of a glass-stoppered bottle shows a dark blue colour. The author has also prepared a black double bromide which is probably the salt Cs_2SbBr_6 . E. G.

Nitrilopentachloro-osmates and the Constitution of Osmiamic Acid. By ALFRED WERNER and K. DINKLAGE (*Ber.*, 1901, 34, 2698—2703).—‘Osmiamic acid’ was discovered by Fritzsche and Struve (*J. pr. Chem.*, 1867, 41, 97) and named by them ‘osman-osmic acid’; its salts were shown by Joly (Abstr., 1891, 1433) to have the formula OsNO_3R , and the constitution $\text{O}:\text{Os}(\cdot\text{OR})\cdot\text{N}:\text{O}$ was proposed for them. Their behaviour towards hydrochloric acid cannot be explained by this formula, and it is suggested that the acid is an imide of perosmic acid, $\text{O} \begin{smallmatrix} \diagup \text{O} \end{smallmatrix} \text{Os} \begin{smallmatrix} \diagdown \text{O} \\ \diagup \text{NH} \end{smallmatrix}$, whilst the salts may be derived from the tautomeric



Potassium nitrilopentachloro-osmate, $(\text{OsNCl}_5)_2\text{K}_2$, prepared by the action of cold hydrochloric acid on potassium osmiamate, is a reddish-brown, crystalline powder which readily dissolves in water with an intense cherry-red colour, and on slow evaporation separates from the solution in ruby-red prisms; it can be partially precipitated from solution by adding hydrochloric acid, decomposes gradually in dilute solution, and more rapidly when heated, and is insoluble in organic solvents. The *ammonium* salt, $(\text{OsNCl}_5)(\text{NH}_4)_2$, prepared by adding ammonium chloride to the liquors of the potassium salt, is a brown-violet crystalline powder, and resembles the potassium salt. The *rubidium* salt, $(\text{OsNCl}_5)\text{Rb}_2$, prepared in a similar way to the ammonium salt, resembles the potassium salt, but is less soluble, and decomposes very rapidly in dilute neutral solution. The *caesium* salt, $(\text{OsNCl}_5)\text{Cs}_2$, is prepared by a similar method, forms a grey powder with a reddish lustre, gives a red solution, but is still less soluble in water than the rubidium salt.

By the action of stannous chloride and hydrochloric acid on the osmiamates, Brizard (this vol., ii, 108) has obtained salts of the formula $(\text{OsCl}_5\text{NH}_2)_2\text{R}_2$, but their relationship with the series now described is not known. T. M. L.

Mineralogical Chemistry.

Crystalline Structure of Silver and Copper Nuggets. By ARCHIBALD LIVERSIDGE (*J. and Proc. Roy. Soc. New South Wales*, 1901, [1900], 34, 255—258).—The examinations were made by etching the polished sections as was previously done with gold and platinum nuggets (*Trans.*, 1897, 71, 1125). A silver nugget from Lake Superior with well-marked crystalline structure had the following composition (analysis by G. A. Waterhouse):

| Ag. | Cu. | Au. | (Fe, Al) ₂ O ₃ . | Gangue. | Total. |
|-------|------|-------|--|---------|--------|
| 97.39 | 0.07 | trace | 0.27 | 1.21 | 98.94 |

In the nuggets containing both silver and copper, from Lake Superior, the silver has been deposited on the copper.

As in the case of the gold and platinum nuggets, there is every indication of the silver and copper nuggets having been deposited from solution, and nothing to indicate that they have undergone fusion, either igneous or hydrothermal. L. J. S.

Crystalline Structure of Gold Nuggets. By ARCHIBALD LIVERSIDGE (*J. and Proc. Roy. Soc. New South Wales*, 1901, [1900], 34, 259—262).—The examination of the crystalline structure of gold nuggets by etching polished sections, as explained in a previous paper (*Trans.*, 1897, 71, 1125), has been extended to specimens from other localities, namely, Victoria, New Zealand and Klondyke.

The structure and appearance of the Klondyke nuggets are quite distinct from those of gold from any other locality. They are very pale in colour, owing to the large amount of silver present. The assays of two gave only 64.550 and 64.622 per cent. of gold, and sp. gr. only 16.23. L. J. S.

Texas Petroleum. By WILLIAM BATTLE PHILLIPS (*Bull. Univ. Texas*, No. 5 [*Univ. Texas Mineral Survey Bull.*, No. 1] 1901, 102 pp.).—A comprehensive account, including the results of several analyses, is given of the occurrence of petroleum in Texas. L. J. S.

Petroleum in Fossiliferous Limestone from Baden. By CARL ENGLER and E. ALBRECHT (*Zeit. angew. Chem.*, 1901, 14, 913—916).—Three samples of yellow to brown thin liquid oil from cavities in fossil shells in Lias limestone at Roth-Malsch, in Baden, gave on analysis the following results: C, 86.59—87.66; H, 12.33—12.92 per cent.; traces of nitrogen and sulphur are also present. Asphalt, pitch, and solid paraffin were separated from the material. This oil is therefore identical with the mineral oil which occurs on a large scale in Nature, and it has probably been derived from the remains of marine organisms. L. J. S.

Analyses of Pyrites. By VASILE C. BUTZUREANU (*Ann. Sci. Univ. Jassy*, 1901, 1, 309—312).—Analyses are given of four samples of massive and crystallised pyrites from Roumania. L. J. S.

Telluride Ores of Cripple Creek and Kalgoorlie. By T. A. RICKARD (*Trans. Amer. Inst. Mining Eng.*, 1901, 30, 708—718).—The telluride ores and minerals of these two gold producing districts, in Colorado and Western Australia respectively, are compared. The following analyses by W. F. Grace are given of petzite from Kalgoorlie; it is iron-black, with sub-conchoidal fracture and sp. gr. 9.

| Ag. | Au. | Te. | Hg. |
|-------|-------|-------|------|
| 40.47 | 24.64 | 34.60 | 0.29 |
| 40.55 | 24.62 | 34.83 | 0.00 |

The mercury is probably due to the presence of admixed coloradoite (HgTe), which resembles petzite in appearance and also occurs at Kalgoorlie. On these grounds, it is suggested that the mineral recently described (Abstr., 1898, ii, 385) under the name kalgoorlite (compare also coolgardite, this vol., ii, 515) is really a mixture of petzite and coloradoite.
L. J. S.

A New Cadmium Mineral. By E. WITTICH and B. NEUMANN (*Centr. Min.*, 1901, 549—551. Compare this vol., ii, 605).—The new mineral, cadmium oxide, CdO, occurs as a black, shining, crystalline encrustation and as powder on a mass of zinc ore with powdery iron oxide from Monte Poni, Sardinia. Analysis of this zinc ore gave the following results:

| ZnO. | SiO ₂ . | Fe ₂ O ₃ . | CaO. | MgO. | Cd. |
|-------|--------------------|----------------------------------|------|------|-----|
| 60.59 | 31.3 | 5.5 | 1.7 | 1.6 | Nil |

The crystals of cadmium oxide are regular octahedra, sometimes with cube planes. H = 3: sp. gr. 6.146. Analysis gave Cd, 87.5; O, 12.5 per cent., corresponding with the values required by the formula CdO.

Black cubes of cadmium oxide of the same characters as the natural crystals were obtained artificially by burning cadmium in oxygen.

Zinc oxide being hexagonal and cadmium oxide cubic, it is probable that these substances are isodimorphous.

Small quantities of cadmium are of fairly wide distribution in zinc minerals, but the only cadmium mineral previously found is greenockite, CdS.
L. J. S.

[Synchysite and Molybdophyllite.] By GUSTAV FLINK (*Bull. Geol. Inst. Univ. Upsala*, 1901 [1900], 5, 81—96).—*Synchysite*.—This new name is applied to a mineral from Narsarsuk, in South Greenland, previously described under the name parisite (Abstr., 1895, ii, 401; 1900, ii, 410). The following new analysis, agreeing closely with that previously given, has been made by R. Mauzelius:

| CO ₂ . | ThO ₂ . | Ce ₂ O ₃ . | (La,Di) ₂ O ₃ . | Y ₂ O ₃ . | CaO. | FeO. |
|-------------------|--------------------|----------------------------------|---------------------------------------|---------------------------------|-------|------|
| 25.99 | 0.30 | 21.98 | 28.67 | 1.18 | 16.63 | 0.11 |
| Total | | | | | | |
| less O for F. | | | | | | |
| F. | | | | | | |
| 5.04 | | | | | | |
| H ₂ O. | | | | | | |
| 2.10 | | | | | | |
| 99.88 | | | | | | |

The following are the main characters which distinguish the two minerals:

| | Synchysite. | Parisite. |
|------------------------|-------------------------------|--|
| Chemical formula | $\text{CeFCa}(\text{CO}_3)_2$ | $(\text{CeF})_2\text{Ca}(\text{CO}_3)_3$ |
| Cleavage | Not original | Distinct basal |
| Sp. gr. | 3.902 | 4.364 |
| Refractive indices ... | ω 1.6742 | 1.569 |
| | ϵ 1.7701 | 1.670 |
| Crystal system | Rhombohedral | Hexagonal |

Molybdophyllite.—This new mineral is of rare occurrence with hausmannite in granular limestone or dolomite at Långbanshyttan, in Wermland, Sweden. It occurs as platy masses with a perfect cleavage in one direction, and has the appearance of mica. Thin plates are perfectly colourless and water-clear, though thicker masses are faintly greyish. It is optically uniaxial and negative. Etching experiments show that it belongs to the hexagonal system. Sp. gr. 4.717. $H = 3-4$. Analysis gives the formula $\text{R}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$, showing it to be distinct from the somewhat similar Swedish mineral, barysilite ($3\text{PbO}, 2\text{SiO}_2$):

| SiO_2 . | PbO . | MgO . | Al_2O_3 . | Na_2O . | K_2O . | H_2O . | Total. |
|------------------|----------------|----------------|---------------------------|-------------------------|------------------------|------------------------|--------|
| 18.15 | 61.09 | 11.71 | 0.46 | 0.82 | 0.69 | 6.32 | 99.24 |
| L. J. S. | | | | | | | |

New Mineral Species found in Baveno Granite. By ETTORE ARTINI (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 139—145).—A new mineral, *bavenite*, occurs on quartz and on orthoclase in the form of fibrous, radiating tufts of slender, white prisms or needles, the extremities being free and terminated by imperfect crystalline faces, and is accompanied by epidote, laumontite, and mica. The mineral, although apparently rhombic, is really monoclinic, each crystal being composed of two individuals twinned along $\{100\}$; [$a:b:c = 1.1751:1:0.7845$; $\beta = 89^\circ 17' 19''$]; it is readily melted by the blow-pipe, and is only slightly attacked by strong acids. Analysis gave:

| SiO_2 . | Al_2O_3 . | CaO . | MgO . | Na_2O . | K_2O . | H_2O . | Total. |
|------------------|---------------------------|----------------|----------------|-------------------------|------------------------|------------------------|--------|
| 56.93 | 15.42 | 24.47 | 0.12 | 0.29 | trace | 2.49 | 99.72 |

These numbers correspond with those required for the formula $\text{Ca}_3\text{Al}_2\text{Si}_6\text{O}_{19} \cdot \text{H}_2\text{O}$.
T. H. P.

Dunite from Koswinsky-Kamen, Urals. By LOUIS DUPARC and FRANCIS PEARCE (*Compt. rend.*, 1901, 133, 476—478).—Several analyses are given of dunite, an olivine-rock occurring as veins penetrating koswite (this vol., ii, 398), and also as large masses in association with this.
L. J. S.

Organic Iodine in the Waters of Salsomaggiore. By C. MONTANARI (*L'Orosi*, 1901, 24, 223—225. Compare Nasini and Anderlini, *Abstr.*, 1900, ii, 489).—The small quantity of iodine in the waters of Salsomaggiore is wholly present in combination with organic matter. Such organic iodine the author considers may be of great importance therapeutically, as is the case with the iodine of the thyroid gland. The water also gives indications of the presence of organic nitrogen, but the quantity of water at the author's disposal was insufficient to allow him to be certain of this.
T. H. P.

Trafalgar Square Well Water. By WALTER W. FISHER (*Analyst*, 1901, 26, 204).—A recent analysis of this water, of which analyses in 1848 (Abel and Rowney, *Q. J. Chem. Soc.*, 1, 97) and 1857 (Campbell, *ibid.*, 9, 22) have been published in this Journal, shows that the composition has not changed substantially during the past forty-four years, but the amount of potassium salts is now much smaller than in the earliest samples. W. W. F.

Alkaline Waters from the Chalk. By WALTER W. FISHER (*Analyst*, 1901, 26, 202—208).—A correction of the earlier abstract (this vol., ii, 627). In view of the fact that alkaline waters are not only drawn from chalk beneath London Clay, but are obtained from other limestones, beneath Gault, Kimmeridge, Oxford, and Lias clays, the author believes that the alkali chlorides, sulphates, and carbonates are dissolved from the chalk itself and do not come from extraneous sources. Chalk obtained under London at depths of 500 and 800 feet contains distinct traces of sodium carbonate as well as chloride and sulphate. Owing to long-continued percolation, soluble salts have washed out from uncovered chalk but remain in the covered deposits where no natural drainage is possible. W. W. F.

Physiological Chemistry.

Minimum Quantity of Oxygen required by Fish ; Poisonous Quantities of Carbon Dioxide in the Water. By J. KUPZIS (*Zeit. Nahr.-Genussm.*, 1901, 4, 631—638).—A record of a large number of experiments with fish (red bream, groundling, whitefish, perch) to ascertain the smallest amount of oxygen required to keep them healthy, and also the influence of carbon dioxide on them. The results are tabulated.

It appears that when the amount of oxygen sinks to 1 c.c. per litre of water, the fish begin to show signs of being unwell, and that they perish when the amount is reduced to 0·8—0·5 c.c. As regards carbon dioxide, this only begins to affect the fish when present to the extent of 0·126 gram per litre, and 0·280 gram was required to kill the fish, except groundling. Carbon dioxide is therefore not likely to cause death to fish in aquaria, &c., as it will never accumulate in anything like these quantities.

L. DE K.

Fat of Human Blood. By MAX ENGELHARDT (*Chem. Centr.*, 1901, ii, 490—491 ; from *Deutsch. Arch. klin. Med.*, 1901, 70, 182—189).—Estimations of fat in human blood were made by Nerking's method. The numbers obtained are smaller than those of previous observers ; in health, the percentage averages 0·194 ; in various cachectic conditions, 0·174.

W. D. H.

Artificial Parthenogenesis. By WILLIAM J. GIES (*Amer. J. Physiol.*, 1901, 6, 53—76). By ALBERT P. MATHEWS (*ibid.*, 142—154).—The first paper deals with the question whether spermatozoa con-

tain an enzyme causing the development of mature ova. The experiments conducted with *Arbacia* led to a negative result. The second paper deals with star-fish eggs, and shows that the stimulus of mechanical agitation will produce the development of embryos. The agitation varied from merely transferring the eggs from one dish to another, to hard shaking in a test-tube. In all cases agitation led to a positive result. The best results were obtained by violent agitation, especially after the eggs had been in sea water for seven hours. The late gastrula stages were produced. W. D. H.

Influence of Food on the Secretion of Enzymes. By PORTIER and BIERRY (*Compt. rend. Soc. Biol.*, 1901, 53, 810—811).—Previous observers have shown that the secretion of enzymes adapts itself to the nature of the food given. The present experiments attempt to discover whether an animal which usually does not secrete a certain ferment will do so when fed on the food on which such a ferment acts. Thus the alimentary canal does not normally secrete inulase; dogs and rabbits were fed on Jerusalem artichokes but no inulase was found. Ducks do not normally secrete lactase; one duck was killed after a fifteen days' diet of lactose, but no lactase was found; another duck, killed ten days later, was found to have abundance of lactase in its intestine. W. D. H.

Salivary Digestion of Carbohydrates in the Stomach. By HENSLEY (*Chem. Centr.*, 1901, ii, 698—699; from *Münch. med. Woch.*, 1901, 48, 1208—1210).—Great importance is attributed to the continuance of salivary digestion in the stomach. Direct observations on the stomach contents of healthy young adults show that the conversion of starch into maltose and soluble dextrins in the stomach is considerable. W. D. H.

Zymogens of the Stomach. By KARL GLAESSNER (*Beitr. chem. Physiol. Path.*, 1901, 1, 1—23, and 24—33).—The first paper describes experiments in which the varying solubilities and resistance to reagents is made use of to separate the zymogens of pepsin and of rennin from each other and from their respective enzymes.

The second paper deals with the distribution of the zymogens; that of rennin is found only at the fundus, and the parietal cells are suggested as its source. The amount of peptic ferment produced at the pyloric end of the stomach is very small; it is called pseudo-pepsin, and is active also in weakly alkaline solutions. W. D. H.

Peptic and Tryptic Digestion of Proteid. By D. LAWROFF (*Zeit. physiol. Chem.*, 1901, 33, 312—328).—The principal result of observations on the auto-digestion of the pig's stomach is that pepsin will, by prolonged action, break up proteids as much as trypsin does. Putrefaction was excluded. W. D. H.

Formation of Ammonia by the Action of Trypsin and Pepsin on Proteids. By S. DZIERZGOWSKI and SERGEI SALASKIN (*Chem. Centr.*, 1901, ii, 645—646; from *Centr. Physiol.*, 26, 249—254).—The quantity of ammonia liberated by the action of natural digestive

fluids on proteids has been determined by Nencki and Zaleski's method. Ammonia is formed by the tryptic as well as by the peptic digestion of fibrin, boiled egg-albumin, crystallised egg albumin, and casein. The amount of ammonia varies with the different proteids, but in every case is greater than that liberated by digestion with dilute acid or alkali and less than that obtained when the albumins are completely decomposed by acids. The quantity of ammonia therefore never corresponds with the total amino-nitrogen of the proteid.

E. W. W.

Decomposition of Proteids by Trypsin. By JUNICHI MOCHIZUKI (*Beitr. chem. Physiol. Path.*, 1901, 1, 44—50).—If in a product of tryptic digestion the total nitrogen is taken as 100, 5.9 parts can be driven off by magnesia, 37.6 are contained in the precipitate produced by phosphotungstic acid, and the remainder is in the filtrate.

W. D. H.

Action of Proteolytic Enzymes on Toxins. By E. R. BALDWIN and P. A. LEVENE (*J. Med. Research*, 1901, 6, 120—134).—Diphtheria and tetanus toxins are digested, and not simply neutralised, by the three proteolytic enzymes, pepsin, trypsin, papain. They are thereby rendered inert. Tuberculin, which is looked on as a nucleo-proteid, is weakened in its action by the digestive ferments mentioned; prolonged digestion with trypsin, but not with pepsin, destroys its activity.

W. D. H.

Digestion in the Small Intestine. By FR. KUTSCHER and J. SEEMANN (*Chem. Centr.*, 1901, ii, 784; from *Centr. Physiol.*, 1901, 15, 275—276).—A dog was fed on meat, and the intestinal contents allowed to flow out of a fistula; these were boiled to prevent further tryptic action. The fluid gave no biuret reaction, but yielded leucine, tyrosine, and lysine.

W. D. H.

Influence of Urotropin on Intestinal Putrefaction. By WILHELM F. LÖBISCH (*Chem. Centr.*, 1901, ii, 705; from *Wien. med. Presse*, 1901).—Urotropin (hexamethylenetetramine) is a good antiseptic. It causes no bad symptoms, and greatly lessens intestinal putrefaction. The ethereal sulphates of the urine are greatly diminished. Under ordinary circumstances, indican is most abundant in the morning urine, and the other ethereal sulphates most abundant in the evening urine.

W. D. H.

Absorption in the Small and Large Intestines. By FELIX REACH (*Pflüger's Archiv*, 1901, 86, 247—258).—Absorption is less active in the large than in the small intestine. Gelatin solution is not so well absorbed as albumose solution in the large intestine; addition of 0.7 per cent. of sodium chloride increases the absorption of gelatin until it equals that of albumoses. The salt stimulates the mucous membrane and increases absorption generally.

In the small intestine, gelatin is a little better absorbed than albumose. Here, salt increases the absorption of albumose but not of gelatin.

Nutritive enemata should therefore be composed of peptonised food with the addition of gelatin and salt. W. D. H.

Digestion and Metabolism in Echinoderms. By OTTO COHN-HEIM (*Zeit. physiol. Chem.*, 1901, 33, 9—54).—Echinoderms (*Holothuria*, &c.) were selected as the objects of experiment, as it was hoped that in such simple animals the phenomena of absorption would be more easily solved than in vertebrates. The absorbed material passes into the body-cavity which represents the circulatory system of higher animals. Diffusion will explain the passage of most material into this fluid, except that an active 'water-transport' must depend on the physiological activity of the intestinal lining cells. The intestine produces a diastatic, an inverting, and, in some cases, a proteolytic ferment. The course of proteid metabolism is by no means clear. *Holothuria* secretes nitrogen only with the fæces. No ammonia is excreted. The production of carbon dioxide is small, and of this one-third leaves the body by the intestine. Small holothurians have a more vigorous metabolism than large ones. W. D. H.

Alcohol and Proteid Metabolism. By RUDOLF ROSEMAN (Pflüger's Archiv, 1901, 86, 307—503).—A long discussion of the results of others. Some new experiments on man are given. The main result is that alcohol, within certain limits, is a proteid sparing food. W. D. H.

Metabolism in the Pig during Feeding with Sugar, Starch, and Molasses. By EMERICH MESSL and WILHELM BERSCH (*Chem. Centr.*, 1901, ii, 784—785; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 1901, 4, 805—921).—The practical outcome of the investigation is the usefulness of molasses as a food for pigs. Full details of the experiments on metabolism in two animals are given. In a young animal, the putting on of flesh was increased, and of fat slightly diminished; in the older animal, this was reversed. W. D. H.

Analogy between Loss of Water and Lowering of Temperature. By ARTHUR W. GREELEY (*Amer. J. Physiol.*, 1901, 6, 122—125).—In *Stentor*, a lowering of temperature produces certain morphological changes, which are the same as those produced by increasing the osmotic pressure of the surrounding medium. On raising the temperature again, the reverse process occurs. In *Spirogyra*, typical plasmolysis may be produced by reduction of the temperature. It is therefore probable that the main effect of lowering the temperature is to cause loss of water. W. D. H.

Oxalic Acid in the Organism. By A. CIPOLLINA (*Chem. Centr.*, 1901, ii, 496; from *Berl. klin. Woch.*, 1901, 38, 544—547).—Human and animal organs contain only small quantities of oxalic acid; most is in the spleen. The total amount is about ten times as great as the daily amount in the urine. The spleen, and perhaps also the liver and muscles, are believed to oxidise uric acid with the formation of oxalic acid. Various foods contain larger amounts of the acid, which is stated to have injurious effects. W. D. H.

Origin of Kynurenic Acid in the Organism. By KARL GLAESSNER and LEO LANGSTEIN (*Beitr. chem. Physiol. Path.*, 1901, 1, 34—43).—The experiments on dogs here recorded are considered to prove with certainty that kynurenic acid is a decomposition product of proteid produced during pancreatic digestion. W. D. H.

Reduction and Action of Aromatic Nitro-compounds [in the Animal Organism]. By KARL WALKO (*Chem. Centr.*, 1901, ii, 597; from *Arch. exp. Path. Pharm.*, 46, 181—196. Compare Rymasz, *Diss. Dorpat*, 1889, and Karplus, *Zeit. klin. Med.*, 22, 210).—When rabbits or dogs are injected with picric acid, by far the greater portion is excreted unchanged, but an amino-compound, a phenol, and a red dye are also found in the urine. The amino-compound is probably picramic acid, and may be detected by means of the azo-dye prepared by extracting with ether, diazotising, and treating with β -naphthol. The phenol is also soluble in ether and gives a brownish-black precipitate with ferric chloride. The red dye is present in far larger quantity than either of the preceding compounds, and is insoluble in ether. These substances do not necessarily result from any vital process in the organism, for they are formed when urine, especially that of dogs, is treated with picric acid, and allowed to remain until ammoniacal fermentation takes place, and also by the action of putrefying albumin, or of the alcoholic extract of dogs' or rabbits' liver on picric acid. Dinitrophenol, *o*-nitrophenol, nitrobenzoic acid, nitrosalicylic acid, nitrobenzaldehyde, nitroacetanilide, trinitronaphthol, nitrourethane, and dinitrohydroxyquinoline do not undergo any change in the animal organism.

The physiological action of picric acid, picramic acid, *o*-nitrophenol, 2:4-dinitrophenol, nitrosalicylic acid, nitrobenzoic acid, nitrobenzaldehyde, and nitrourethane is described in the original paper.

Under certain conditions, the paralysing action of strychnine on the peripheral nerves may become more pronounced, and in the case of the nitro-derivatives, dinitrostrychnine, and 'cacostrychnine,' this effect is predominant. Dinitrobrucine and 'cacotheline' also exert an action resembling that of curare. The nitro-derivative of thebaine, prepared by the action of nitric acid on thebaine at 60°, forms a pale yellow precipitate and has a physiological action different from that of thebaine itself. Nitroatropine and nitrosanguinarine have no effect on frogs. These results show that no common physiological action can be ascribed to nitro-compounds. E. W. W.

Syntheses in the Animal Organism. III. Oxidation Products of Citral in the Organism and some Cyclic Isomerides. By HERMANN HILDEBRANDT (*Chem. Centr.*, 1901, ii, 597—599; from *Arch. exp. Path. Pharm.*, 46, 261—273).—The mother liquor of the dibasic acid, $C_{10}H_{14}O_4$, found in the urine of rabbits after feeding with citral (this vol., ii, 180) is neither a glycuronic acid compound, since it is soluble in ether and does not reduce cupric oxide, nor geranic acid, $C_{10}H_{16}O_2$, for on digesting with a 65—70 per cent. solution of sulphuric acid it does not form α -cyclogeranic acid but yields, on the contrary, a dibasic acid, $C_{10}H_{14}O_4$. This acid separates in white,

crystalline masses, melts at 96° , is easily soluble in ether or hot light petroleum, but only slightly so in cold light petroleum and combines with 1 mol. of bromine. The original amorphous acid is probably a chain compound, and is converted by the action of the acid into a crystalline, cyclic isomeride. Since both these acids are also found in the urine after feeding with geranic acid, it must be assumed that citral is first oxidised to geranic acid in the organism. Attempts to convert the crystalline acid, $C_{10}H_{14}O_4$, melting at 187° , into a cyclic isomeride by the action of dilute acid failed, and similarly a cyclic isomeride of the crystalline acid obtained after administering α - and β -cyclogeranic acids could not be prepared. The cyclogeranic acids are, in fact, almost completely oxidised in the organism, and for the same reason cyclocitral and α - and β -geranic acids are much less poisonous than the corresponding chain compounds.

The mother liquor of the crystalline dibasic acid from which the oily isomeride has been removed, still contains the glycuronic acid compound of citral. By boiling this compound with dilute sulphuric acid and distilling in steam, a yellow oil is obtained. This oil is neither citral nor *p*-cymene, since when administered to rabbits neither the acid $C_{10}H_{14}O_4$ nor cumic acid, but a monobasic acid, $C_{10}H_{12}O_2$, is found in the urine. This acid crystallises from alcohol in long, slender needles, melts at 110° , is easily soluble in ether, and is not volatile in steam; it is not a derivative of cyclocitral, since it is not found in the urine after feeding with this substance. It is isomeric with cumic acid and hence probably the glycuronic acid compound of citral is related to *p*-cymene.

E. W. W.

First Appearance of Aldehydase in the Mammalian Embryo. By MARTIN JACOBY (*Zeit. physiol. Chem.*, 1901, 33, 128—130).—Previous observers have associated the oxidising ferments with nucleoproteids, or with nuclear activity. It is, however, certainly the case that no oxydase, or at least no aldehydase, can be obtained from rapidly growing young mammalian embryos. In the pig embryo, it is not found until it attains the length of 9 cm. Possibly it may be present in the form of a zymogen at earlier dates.

W. D. H.

The Action of Serum-globulin on the Coagulation of Muscle Plasma. By KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1901, 1, 78—79).—Serum-globulin possesses the power of hastening the coagulation of muscle plasma and the precipitation of its essential proteids. This, however, is the property of the eu-globulin fraction and not of the pseudo-globulin.

W. D. H.

Autolysis of the Lung. By MARTIN JACOBY (*Zeit. physiol. Chem.*, 1901, 33, 126—127).—Previous observers have noticed autolysis in various organs, liver, &c. The lungs of pigs were investigated to ascertain if a similar process occurs there. The products of proteid decomposition (leucine, tyrosine, &c.) were found in the lung tissue after removal from the body, bacterial action being excluded. Autolysis thus occurs in the lung and, indeed, may be regarded as an important physiological cell-function.

W. D. H.

Formation of Uric Acid in the Liver of Birds. By KATHARINA KOWALEWSKI and SERGEI SALASKIN (*Zeit. physiol. Chem.*, 1901, 33, 210—222).—The experiments described show that the liver takes a direct share in the formation of uric acid in birds, and, indeed, may be considered as the place where its synthesis occurs. The materials for its formation are not only ammonium lactate and ammonium salts of other organic acids, but may include such substances as arginine.
W. D. H.

[**Thyreo-globulin.**] By F. BLUM (*Zeit. physiol. Chem.*, 1901, 33, 345—346).—Polemical: a reply to A. Oswald (this vol., ii, 461).
J. J. S.

Stimulation and Paralysis of Nerve-cells and Nerve-endings. By JOHN W. LANGLEY (*J. Physiol.*, 1901, 27, 224—235).—The main action of nicotine in nerve-cells is that of stimulation, but differences are noted in different animals. It does not stimulate the nerve-endings of preganglionic fibres.
W. D. H.

Poisonous Effect of pure Sodium Chloride on Nerve-muscle Preparations. By HARVEY CUSHING (*Amer. J. Physiol.*, 1901, 6, 77—90).—Pure solutions of sodium chloride in increasing strengths produced an increasingly harmful effect on nerve-muscle preparations, This primarily affects the nerve-endings, and may be counteracted by 'physiologically balanced' salt solutions. An excess of calcium ions may produce an effect resembling *rigor mortis*.
W. D. H.

Human Colostrum. By HENRI LAJOUX (*J. Pharm. Chim.*, 1901, [vi], 14, 145—151, and 197—203).—The colostrum contains a larger proportion of nitrogenous substances than the milk, but the quantity rapidly diminishes; it also contains less lactose and a greater proportion of mineral constituents. The amount of fat is variable but gradually increases. The total solids, fat, nitrogenous substances, lactose, ash, and the refractive index of the fat were determined on ten samples of colostrum, and the results are tabulated in the original; these analyses indicate the variability in the duration of the colostrum period; at the end of seven or eight days, the lacteal secretion of one subject had attained all the characters of milk, whilst that of another still possessed on the tenth day the viscosity and other properties of colostrum. The index of refraction of the fat diminishes as the time from parturition increases.

When the colostrum is treated with alcohol or excess of acetic acid, it yields a white, gelatinous, mucous substance, which, however, in exceptional cases, is deposited spontaneously. This precipitate is soluble in boiling dilute hydrochloric or sulphuric acid, with formation of an acid albumin and a substance which reduces Fehling's solution. The substance precipitated by alcohol is found to contain considerably less nitrogen than would be the case if it consisted only of albumin and casein. These facts show that the colostrum contains normally a true mucin, for which the author proposes the name *lactomucin*.
E. G.

Iron in Human Milk. By ADOLF JOLLES and JOSEF K. FRIEDJUNG (*Chem. Centr.*, 1901, ii, 596; from *Arch. exp. Path. Pharm.*, 1901, 46, 247—260).—The average amount of iron in thirty specimens of human

milk is 5.09 mg. per litre. Non-hygienic conditions and ill-health cause a diminution. Ill-health of the child is a result, even when the mother is otherwise healthy. Various kinds of artificial human milk are also poor in iron. W. D. H.

Composition of Cows' Milk in different stages of Milking. By P. HARDY (*Chem. Centr.*, 1901, ii, 645; from *Bull. Assoc. belge Chim.*, 1901, 15, 228—229).—In one experiment the first litre of milk drawn from the udder contained 3.5 per cent. of fat, the second, 3.75, the third, 3.8, the fourth, 4.2 per cent.; the solids rose from 11.85 to 12.25, the ash from 0.72 to 0.74 per cent. In another experiment, the result was 2.8, 4.15, 4.25, 5.1 per cent. of fat, 11.75—13.66 per cent. of solids, and 0.72—0.74 per cent. of ash. The milk of a third cow, which was collected half a litre at the time, showed 2.2, 2.9, 3.5, 3.75, 3.8, 3.9, 4.65 per cent. of fat, the solids rising from 10.52 to 12.70, and the ash from 0.74 to 0.75 per cent. The composition of the serum remains the same. L. DE K.

The 'Skin' of Warmed Milk. By R. JAMISON and A. F. HERTZ (*J. Physiol.*, 1901, 27, 26—30).—The formation of a skin on warming is not characteristic of milk, but takes place in any proteid solution containing emulsified fat or paraffin. The film is formed of unchanged, dried proteid in the case of non-coagulable proteid, and in that of coagulable proteid if the temperature is kept below their coagulating point. If the temperature is higher, part of the proteid in the latter case is coagulated. The fat or paraffin globules are entangled in the film. Drying is an essential condition for the formation of the film. W. D. H.

Oxidising Ferment contained in Pus. By DIOSCORIDE VITALI (*L'Orosi*, 1901, 24, 253—263).—The author finds that pus contains an oxidising enzyme which can be extracted by the action either of water or of not too concentrated acetic acid or of glycerol diluted with about half its volume of water, the pus being first triturated with glass until a homogeneous, pasty mass is obtained, the solvent then added, and after further trituration, the mass filtered. The filtered liquid thus prepared contains the oxydase, as it imparts an azure-blue colour to guaiacum resin. The action of the enzyme is destroyed by dilute hydrocyanic acid, chloroform, hydroxylamine, quinol, or pyrogallol, but is not influenced by aqueous phenol, thymol, or mercuric chloride. Like the vegetable oxydases, this enzyme contains a small proportion of manganese. T. H. P.

Electrometric Determination of the Acidity of Urine. By LADISLAUS VON RHORER (*Pflüger's Archiv*, 1901, 86, 586—602).—*E.M.F.* determinations on the lines indicated by Bugarszky and Liebermann (*Abstr.*, 1898, i, 716) show that the concentration of H^+ ions in urine is about 30×10^{-7} . The author considers that they are primarily produced by the dissociation of the dihydrogen phosphates. The urine behaves like an acid which, in $N/30$ concentration, is dissociated to the extent of 1/100 per cent. J. C. P.

Red Colouring Matter occurring in Urine after administration of Pyramidone. By MAX JAFFE (*Ber.*, 1901, 34, 2737—2741).—The

colouring matter is identical with Knorr's rubazonic acid,

$$\begin{array}{c} \text{NPh} \cdot \text{CO} \\ | \\ \text{N} = \text{CMe} \end{array} \text{CH} \cdot \text{N} : \text{C} \begin{array}{c} \text{CO} - \text{NPh} \\ | \\ \text{CMe} : \text{N} \end{array} \quad (\text{Abstr., 1887, 602}). \quad \text{T. M. L.}$$

Lecithin in Tuberculosis. By H. CLAUDE and ALY ZAKY (*Compt. rend.*, 1901, 133, 486—488; *Compt. rend. Soc. Biol.*, 1901, 53, 821—823).—Lecithin is stated to have a specific action on the elimination of phosphates in the urine, and a beneficial action on nitrogenous metabolism; it is therefore recommended as an adjuvant to other means of treating tuberculosis. W. D. H.

Influence of Lecithin on Urinary Constituents. By ALY ZAKY (*Compt. rend. Soc. Biol.*, 1901, 53, 830—832).—In man, lecithin produces, as in animals, an increase of total nitrogen, of urea, and of the coefficient of utilised nitrogen, and a diminution of the phosphoric acid, and usually of the uric acid in the urine. W. D. H.

Ricin Immunity. By MARTIN JACOBY (*Beitr. chem. Physiol. Path.*, 1901, 1, 51—77).—The toxin of ricin and the agglutinin go together; the immunising agent, antiricin, is here studied in a number of experiments conducted according to Ehrlich's views. The existence of ricin toxoids is established; these are removable by artificial gastric digestion. W. D. H.

Arsenic in the Organs of the Body. By C. HÖDLMOSE (Zeit. physiol. Chem., 1901, 33, 329—344).—Gautier has stated that, normally, certain parts of the body (hair, thyroid, menstrual blood, &c.) contain arsenic (Abstr., 1900, ii, 152). These observations are not confirmed. Arsenic does not appear to be a normal constituent of the body. W. D. H.

Localisation and Dissemination of Antimony in the Animal Organism. By G. POUCHET (*Compt. rend.*, 1901, 133, 526—527).—When antimony in the form of tartar emetic is administered for a long time to rabbits and dogs by ingestion, it tends to accumulate in the digestive tract and is found only in very small quantities in the organs and other parts of the body. It therefore differs markedly from arsenic. If antimony is administered with small quantities of arsenic, the toxic effect of the latter seems to be increased, but the distribution of the two elements in the organism is not affected. C. H. B.

Physiological Action of Suprarenal Extract. By JOHN N. LANGLEY (*J. Physiol.*, 1901, 27, 237—256).—Suprarenal extract causes a brief but active secretion of the salivary and lacrimal glands. This is not affected by degeneration of the post-ganglionic fibres of the superior cervical ganglion, or by small doses of atropine, but after a large dose of atropine, there is no secretion caused by the extract. It has no certain effect on the secretion of sweat. It increases secretion of bile. It acts differently on different involuntary muscular organs, causing, for instance, inhibition of the bladder, stomach, gall bladder, &c., and contraction of the anal sphincters, uterus, and blood vessels. The theory that the extract acts on sympathetic nerve-endings breaks down in various instances. If its action is a direct

one on unstriated muscle, the difference must depend on intrinsic differences in the muscle which are at present unknown. W. D. H.

Comparative Investigations of the Pharmacological Actions of some Purine Derivatives. By OSWALD SCHMIEDEBERG (*Ber.*, 1901, 34, 2550—2559).—Experiments were made with frogs and rabbits; the drugs were dissolved in either water or sodium carbonate solution, and were administered either internally or by injection into the blood. The action of caffeine and theobromine is already known to be twofold. In the first place, they act on the central nervous system, producing an increased sensibility to external stimulus, developing into tetanus as the dose is increased, and culminating in paralysis when the dose is large. Secondly, they act on the muscles, facilitating the contraction of these at first, but producing muscular rigor when the dose is larger; the rigor may be local when the drug has been injected into the blood at a particular spot. Under the microscope, they are seen to coagulate the muscle-plasma. The relative degree of these two actions varies from substance to substance; with theobromine, the action on the muscles is greater in proportion to that on the nervous system than it is with caffeine. Parallel with the action on the muscles is a diuretic action, the two increasing together.

The nervous action depends on the presence of nitrogen in the molecule, for it is exhibited also by ammonia and ammonium salts. On the other hand, the muscular action is characteristic of the purine ring. Purine itself exhibits both actions. Introduction of oxygen or alkyl groups affects the degree of the two actions, both absolutely and relatively; no regularities could be observed in this respect, however. Such regularities as exist are probably masked by the fact that, owing to the difference in solubility and other causes, the rate at which the drug penetrates to the nerve cells and muscle fibres varies very much from case to case. Probably it is for some such reason that 7-oxypurine produces no muscular rigor and 2-oxypurine no tetanus, whereas with the 1:6-dimethyl derivative of the first and 1:3-dimethyl derivative of the second the missing action is manifested; the first two substances are insoluble in water and only slightly soluble in aqueous sodium carbonate, whereas the second two dissolve readily in water. The introduction of alkyloxy-groups produces a hypnotic or narcotic action, which may almost mask the tetanus. Several peculiarities were observed; for instance, 3:4:6-trimethylxanthine is only slightly active whilst 1:4:6-trimethylxanthine (caffeine) is much more so, and uric acid is not active, whilst its 1:3:4:6-tetramethyl derivative is.

Experiments were made with the following substances:—Purine 7-oxypurine (hypoxanthine), 1:6-dimethylhypoxanthine, 2-oxypurine, 1:3-dimethyl-2-oxypurine, 1:4:6-trimethyl-6:7-dihydro-5-oxypurine (deoxycaffeine), 5:7-dioxypurine (xanthine), 4-methylxanthine, 1-methylxanthine (heteroxanthine), 1:6-dimethylxanthine (theobromine), 4:6-dimethylxanthine (theophylline), 1:6-dimethylxanthine (paraxanthine), 3:4:6-trimethylxanthine, 1:4:6-trimethylxanthine (caffeine), 4-methyl-1:6-diethylxanthine, 1:2:4:6-tetramethylxanthine (2-methylcaffeine), 2:7-dioxypurine, 1:3-dimethyl-2:7-di-

oxypurine, 1:3:6-trimethyl-2:7-dioxypurine (*isocaffeine*), 2:5:7-trioxypurine (uric acid), and 1:3:4:6-tetramethyluric acid.

C. F. B.

Gelatin Fibres. By E. WAYMOUTH REID (*J. Physiol.*, 1901, 27, 161—173).—The experiments recorded lead to the conclusion that it is fallacious to take the filtrate of a physiological fluid through a gelatin membrane as identical with the original fluid in all respects except that of concentration of colloids. These membranes hold back some substances in ordinary solution, and the extent to which they are retained will have to be determined in each case by those who desire to use such filters for quantitative purposes.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Physiology of *Bacillus Pyocyaneus*. By OSCAR LOEW and YOSHINAI KOZAI (*Bull. Coll. Agr. Tokyo Imp. Univ.*, 1901, 4, 227—236).—As regards the nutrition of *B. pyocyaneus*, it was found that asparagine is more suitable than leucine, tyrosine, glycine, hydantoin, or creatine, and that acetates are better than tartrates. Acetates and glycerol promote the formation of mucus, but not to the same extent as broth.

In the production of the bacteriolytic enzyme, peptone was found to be the best nutrient; mucus is not formed to any extent. The presence of a little glycerol is beneficial, but increasing the amount of magnesium sulphate to 1 per cent. is without advantage.

N. H. J. M.

Biochemical Studies on the Tubercle Bacillus. By P. A. LEVENE (*J. Med. Research*, 1901, 6, 135—144).—Elementary analysis of the tubercle bacilli prepared on different media gave widely different results, especially in the amount of alcohol-ether extract. Differences were also observed in the amounts of proteid and of free nucleic acid present. By fractional heat-coagulation, the proteid material can be separated into three substances, each of which contains phosphorus. The nucleic acids separated vary much in composition; some of the preparations made are looked on as purer than the others. The only carbohydrate studied was one which closely resembles glycogen; this appears to be always present.

W. D. H.

Albumin-forming Bacteria. By GERLACH and VOGEL (*Centr. Bakt. Par.*, 1901, [ii], 7, 609—623).—Soil and stable manure contain several varieties of motile, non-spore-forming bacteria which are capable of converting the nitrogen of nitrates, nitrites, ammonium salts, and urea into insoluble proteids. Cultivated in a medium containing mineral salts, 0.5 per cent. of dextrose, and 0.3 per cent. of sodium nitrate, a certain amount of nitrite is formed, but after 5—10 days neither nitrate nor nitrite remains, whilst the total nitrogen

of the solution is unaltered, the whole of it being present in the insoluble proteids formed. No ammonia is produced. The nitrogen of ammonium salts is less readily assimilated and that of urea still less readily. In neither case is there any formation of nitrate or nitrite. When a solution containing urea is inoculated* with these bacteria and with a species capable of converting urea into ammonium carbonate, a certain amount of the ammonia produced is utilised by the proteid-forming bacteria, but a considerable loss takes place by evaporation of the ammonia from the solution, so that the presence of proteid-forming bacteria in stable manure is not sufficient to prevent loss of ammonia in this way. In the presence of denitrifying organisms, practically the whole of the nitrogen of sodium nitrate is evolved as nitrogen, the denitrifying action proceeding much more rapidly than the conversion of the nitrogen of nitrates into proteid. When nitrate is added to garden soil containing some straw as a source of carbon, a similar action goes on; soil contains both denitrifying and proteid-forming organisms, and the result is not affected by inoculating with either or both species.

A. H.

Decomposition of Fodder and Food by Micro-organisms.

I. Organisms Destroying Fats. By JOSEF KÖNIG, ALB SPIECKERMANN, and W. BREMER (*Zeit. Nahr.-Genussm.*, 1901, 4, 721—744 and 769—780).—A chemical and bacteriological investigation of the changes undergone by cottonseed-meal when decomposed by micro-organisms. Three samples of meal each contained moulds and bacteria; the moulds only grew when the meal contained more than 14 per cent. of moisture. The growth of the moulds was accompanied by a decomposition of the fats and the nitrogen-free extractives. The bacteria, on the other hand, had a stronger action on the proteids. Experiments with pure cultures showed that the moulds decompose, not only fats, but also fatty acids, both being apparently converted directly into water and carbon dioxide.

R. H. P.

Monilia Sitophila, a Technical Mould from Java. By F. A. F. C. WENT (*Centr. Bakt. Par.*, 1901, [ii], 7, 544—550 and 591—598. Compare this vol., ii, 411).—This mould brings about hydrolysis of fats, peptonisation and further decomposition of proteids and amylolysis, and penetrates the walls of vegetable cells, breaking up the cellulose. The best single medium for its cultivation is peptone. In presence of ammonium nitrate, as a source of nitrogen, it can derive its carbon from raffinose, maltose, dextrose, starch, commercial lævulose, as well as in a less degree from many other carbohydrates and allied compounds. In a similar manner, when the source of carbon is dextrose, the best source of nitrogen is found to be peptone or tyrosine. Glycerol, by itself, is only very slowly assimilated, but when both glycerol and raffinose are employed, the yield is far greater than when raffinose alone is present. It seems probable that the glycerol is oxidised, whilst the raffinose is assimilated for the purpose of mycelium formation. The mould only develops sparingly under anaërobic conditions, forming alcohol and esters, the nature of which could not be determined.

A. H.

Agglutination of Yeast. By H. P. BARENDRECHT (*Centr. Bakt. Par.*, 1901, [ii], 7, 623—627).—Some varieties of yeast are rapidly agglutinated in the presence of acids. The optimum concentration of acid varies slightly, but corresponds on the average with $N/300$ sulphuric acid. The action appears to be a function of the concentration of the hydrogen ions, since weak acids, such as acetic acid, must be present in larger amount, and their action is much diminished by the presence of a salt of the same acid. When the amount of acid is increased beyond the optimum, the agglutination takes place more slowly and less perfectly. Different varieties of yeast show considerable differences in the ease with which they are agglutinated, and the nature of the medium in which they have been cultivated also modifies the result, ammonium salts being favourable to the occurrence of agglutination. The agglutination which sometimes occurs in the manufacture of pressed yeast is not due to this cause, but is produced by the viscous substances formed from sucrose by an organism (*Leuconostoc agglutinans*) which is always found in such samples. A. H.

Experiments with Yeast Cells in Concentrated Saline Solutions. By CHARLES CLERFEYT (*Bull. Acad. Roy. Belg.*, 1901, 23, 337—348).—Yeast cells can be accustomed to grow in concentrated saline solutions; those accustomed to any one particular salt will grow at a slower rate than ordinary yeast cells in a solution of another salt. In these experiments, the electropositive ion had the greater influence. R. H. P.

[Proteolytic Enzyme from Yeast.] **A Reply to Kutscher.** By MARTIN HAHN and L. GERET (*Zeit. physiol. Chem.*, 1901, 33, 385—389. Compare this vol., ii, 466, 523).—The different results obtained by the authors and by Kutscher may be due to the fact that they themselves used filtered solutions of enzymes free from cells, whereas Kutscher used the enzyme in the presence of dead cells. The proteolytic enzyme of yeast—yeast trypsin of Kutscher, yeast endotrypsin of the authors—differs essentially from pancreatic trypsin in the fact that it becomes much less active in the presence of acid. J. J. S.

Distribution of Acidity in Stems, Leaves, and Flowers. By A. ASTRUC (*Compt. rend.*, 1901, 133, 491—493).—The study of the acidity of plants, which was hitherto confined chiefly to oil-yielding plants, has been extended by the author to a large number of widely different families.

It was found that the acidity of the stems diminishes with the distance from the top of the stem, and that the acidity of the leaves especially the growing zone, is greater than that of the stems. In the case of flowers, the acidity diminishes as development proceeds.

The most recent growth always shows the greatest acidity, and there is a close relation between the production of acids on the one hand and of intensity of growth on the other. N. H. J. M.

§ **Formation of Acids in Plants.** By MARCELLIN P. E. BERTHELOT and GEORGES ANDRÉ (*Compt. rend.*, 1901, 133, 502—504).—The total equivalent of the acids present in a plant can only be ascertained b

determining the alkalinity of the ash of the plant, and adding the value thus found to the acidity of the juice of the plant as determined directly by titration. C. H. B.

Occurrence of Organic Iron Compounds in Plants. By U. SUZUKI (*Bull. Coll. Agr. Tokyo Imp. Univ.*, 1901, 4, 260—266).—The seeds and leaves of *Polygonum tinctorium* (1 *a* and *b*) and of *Indigofera tinctoria* (2 *a* and *b*) were found to contain 2.84, 15.5, 4.0, and 4.3 per cent. of crude ash respectively of the following composition :

| | | K ₂ O. | Na ₂ O. | CaO. | MgO. | Fe ₂ O ₃ . | P ₂ O ₅ . | SO ₃ . | SiO ₂ . |
|-----|-----------|-------------------|--------------------|------|-------|----------------------------------|---------------------------------|-------------------|--------------------|
| 1 { | <i>a.</i> | 21.5 | 2.4 | 5.1 | 15.2 | 12.1 | 41.1 | 4.10 | 0.35 |
| | <i>b.</i> | 21.40 | 6.0 | 39.1 | 12.30 | 3.11 | 4.13 | 4.77 | 1.75 |
| 2 { | <i>a.</i> | 18.7 | 4.2 | 11.0 | 9.9 | 12.0 | 34.2 | 2.4 | 3.1 |
| | <i>b.</i> | 17.80 | 2.0 | 37.0 | 6.4 | 4.8 | 3.50 | 3.80 | 6.25 |

The ethereal, alcoholic, and aqueous extracts of the dried leaves and seeds were found to be free from iron. Solutions of sodium chloride extracted only traces of iron or none at all. The greater portion of the iron (60—70 per cent.) is present in a nuclein-like substance which is precipitated by dilute acetic acid from extracts with dilute alkali ; the precipitate contains N 10.4 and Fe 0.5 per cent. When subjected to artificial pepsin digestion, a portion of the proteid dissolved, and on precipitating the solution with alcohol, the products still contained iron. The residue, insoluble in pepsin, contains N 5—10 and Fe 0.5—1.0 per cent.

The iron compound differs from hæmatogen in being partially dissolved by artificial pepsin digestion ; both the dissolved and undissolved portions liberate small quantities of iron when treated with 0.2 per cent. hydrochloric acid. It is also much more sparingly soluble in dilute ammonia than hæmatogen. N. H. J. M.

Chemical Changes in Apples during Ripening. By RICHARD OTTO (*Chem. Centr.*, 1901, ii, 553 ; from *Proskauer Obstbau-Zeit.*, 1901, July).—The following changes have been found to take place in apples when allowed to ripen on the tree or when stored. The amounts of water and ash of the dry substance decrease as the fruit matures, whilst, on the other hand, the quantity of dry substance increases. Unripe apples contain a maximum of about 4 per cent. of starch which at first only slowly, but afterwards more rapidly, decreases until it disappears entirely in the ripe fruit. The amount of cellulose does not change during the initial stages of maturing, and the content of sucrose is also not affected by ripening but decreases on prolonged storing. The nitrogenous substances attain a maximum in the ripe apple but decrease on storing. The sp. gr. of apple must increases on keeping, whilst the total acids calculated as malic acid and the small quantity of pectic acid decrease. The quantity of sugar estimated by Öchsle's method is on the average 0.7—0.9 per cent. less than that of the total sugar, dextrose, and extract determined by Allihn's method ; the data obtained by both methods show a constant increase during the storing of the must. E. W. W.

Bark of Robinia Pseudacacia. By FREDERICK B. POWER (*Pharm. J.*, 1901, [iv], 13, 258—261, and 275—279).—The author has shown (*Pharm. Rundschau*, 1890, 29—38) that the bark of *Robinia Pseudacacia* contains a toxic proteid, for which he now proposes the name *robin*. This substance has an acid reaction, is soluble in water and salt solutions, and is reprecipitated by acids; it is coagulated by heat with complete loss of its poisonous properties. It gives the usual colour reactions of proteids, and yields about 4 per cent. of ash which contains a considerable amount of iron. It also possesses the properties of an enzyme, effecting the hydrolysis of both amygdalin and potassium myronate. It is capable of coagulating the casein of milk, and of agglutinating the red blood corpuscles of certain animals.

The bark also contains one or more substances of an alkaloidal nature which could not be isolated owing to their decomposition, with formation of ammonia and small quantities of an amine. When an extract of the bark is boiled with hydrochloric acid, syringic acid and dextrose are produced, together with a red, amorphous substance which is probably syringenin. Tannic acid, some amorphous colouring matter, fat, and resin are also found in the bark.

The leaves of the plant appear to contain neither a soluble proteid nor an alkaloid. E. G.

Physiological Significance of Colchicine in different varieties of Colchicum and Merendera. By GIACOMO ALBO (*Arch. Sci. Phys. Nat. Genève*, 1901, [iv], 12, 227—236).—Colchicine was found to occur, not only in *Colchicum autumnale*, but also in *C. laetum*, *C. variegatum*, *C. Bisignani*, *C. Cupani*, *C. veratrifolium*, *C. Bivonae*, *C. persicum*, *C. neapolitanum*, *C. montanum v. Bertolini*, *C. montanum v. angustifolium*, and *C. autumnale v. fl. purpureus*. It also occurs in the leaves of *Merendera caucasica* and *M. sobolifera*, its localisation being almost identical with that of *Colchicum*. The amount of the alkaloid extracted from *C. Cupani* was 0.464 per cent.

In growing plants, the alkaloid tends to migrate to the newly-formed portions and accumulates in the seeds, especially during maturation; it is localised in the parenchymatous cells of the placenta, and is never found in dead cells or in intracellular spaces (compare *Arch. Ital. Biol.*, 33, 73).

The conclusion is drawn that colchicine is not a waste product of protoplasmic activity, but that it is a reserve substance which contributes to the nutrition of the plant. N. H. J. M.

Rôle of Oxydase in the preparation of Commercial Black Tea. By K. ASÔ (*Bull. Coll. Agr. Tokyo Imp. Univ.*, 1901, 4, 254—259).—The colour of black tea is shown to be produced by the action of oxydase on tannin. In the case of green tea, the oxydase is destroyed during the first treatment in its preparation.

Tea leaves contain nucleo-proteids in which both iron and manganese are present. N. H. J. M.

Tea Plant. By U. SUZUKI (*Bull. Coll. Agr. Tokyo Imp. Univ.*, 1901, 4, 288—296).—Theine is not present in tea seeds, and cannot be obtained from the proteids of the seeds by the action of hydrochloric

acid. The production of theine during germination must be due to a far-reaching transformation of the products of metabolism. Etiolated and normal shoots contain about the same amounts of theine. Cotyledons of germinating seedlings contain very little theine; stems and roots, moderate amounts.

The largest amounts of theine are contained in the leaves, and the quantity present is nearly proportional to their development. Sodium nitrate has no marked effect in increasing the amount of theine; this makes it probable that theine is a product of katabolism, and not of synthesis like asparagine.

The dormant buds are moderately rich in theine, but the bark and trunk of the tea plant only contain doubtful traces. N. H. J. M.

Localisation of Theine in Tea Leaves. By U. SUZUKI (*Bull. Coll. Agr. Tokyo Imp. Univ.*, 1901, 4, 297—298).—On immersing a section of a tea leaf in 0.5 per cent. theine solution, a very marked formation of proteosomes was observed in the cells of the spongy and palisade tissues. As there was no production of proteosomes in the epidermal cells, it is evident that these cells are free from active proteid, and contain the whole of the theine of the leaves. This conclusion was proved to be caused by keeping a section of a tea leaf in a tannin solution (about 3.4 per cent.) for 2 days; a voluminous precipitate consisting of minute globules was produced in the epidermal cells, whilst the other tissues showed only a slight turbidity. The precipitate dissolved in very dilute ammonia and consisted therefore of theine tannate. N. H. J. M.

Occurrence of Paraffins in Tobacco Leaf. By RICHARD KISSLING (*Chem. Zeit.*, 1901, 25, 684).—The author dissents from the view expressed by Thorpe and Holmes (*Proc.*, 1901, 17, 170), that the waxy substance which he previously described (*Abstr.*, 1884, 173) as an ester of a high fatty acid can be a mixture of paraffins. J. J. S.

Cigar Smoke. By JOSEF HABERMANN (*Zeit. physiol. Chem.*, 1901, 33, 55—125. Compare Kissling, *Abstr.*, 1882, 906; Thoms, *Abstr.*, 1900, ii, 428).—The method employed for collecting the products of combustion was somewhat similar to that used by Kissling, except that the burning was intermittent and not continuous. This was accomplished by the aid of a suitable aspirator, which is described in the paper.

The results obtained indicate that only a small portion of the nicotine passes into the aspirated smoke. For the estimation of nicotine, the author has employed Kissling's method, using, however, methyl-orange instead of rosolic acid as indicator.

The smoke from each of the different kinds of cigars employed contained hydrogen sulphide and carbon monoxide, but hydrogen cyanide was not detected, although there is a possibility that some small amount was formed, and condensed before reaching the flask in which the test was made. The amount of carbon dioxide was on the average four times that of the monoxide, and the shape of the cigar does not appear to affect this ratio.

A portion of the basic substances found in the smoke and "ends"

probably consists of nitrogenous compounds formed by the destructive distillation of proteids in the cigars. J. J. S.

Acids Soluble in Ether contained in Molasses Residues. By ALEXANDER HERZFELD (*Zeit. Ver. deut. Zuckerind.*, 1901, 720—745).—The residues from the desaccharification of molasses by the strontia process furnish a suitable sugar-free material for studying the non-saccharine components of molasses. The author discusses the literature of the subject, and then describes his own experiments made on various samples of such residues. Of one sample, 20·6 per cent. of the dry substance was found to dissolve in ether, and of the ether-soluble portion, 4·92 per cent. consisted of formic acid, 20·88 of acetic acid, 20·9 of lactic acid, and about 3 per cent. of propionic, valeric, and butyric acids; succinic acid is also present. The methods of separating and determining these acids are described. T. H. P.

Banana Soils of Jamaica. By HERBERT H. COUSINS (*Bull. Bot. Dept. Jamaica*, 1901, 8, 145—154).—Mechanical and chemical analyses have been made of a number of Jamaica soils. The samples of surface soil (9 inches) were all free from stones and contained very little gravel, being mostly fine silt and sand with some clay (trace to 17·45 per cent.). The following results, per cent. in dry soil passing 3 mm. sieve, are given:

| N. | Humus (sol. in ammonia). | Soluble in HCl. | | | | Available. | |
|----------|--------------------------------|-------------------|-------|---------------------------------|--|-------------------|---------------------------------|
| | | K ₂ O. | CaO. | P ₂ O ₅ . | CO ₂ as CaCO ₃ . | K ₂ O. | P ₂ O ₅ . |
| 1. 0·196 | 3·58 | 0·925 | 1·62 | 0·138 | 0·506 | 0·0272 | 0·0096 |
| 2. 0·143 | 4·96 | 0·645 | 13·59 | 0·157 | 23·33 | 0·0024 | 0·0048 |
| 3. 0·116 | 2·50 | 0·745 | 17·22 | 0·122 | 26·92 | 0·0048 | 0·0008 |
| 4. 0·211 | 3·15 | 0·291 | 0·24 | 0·025 | 0·12 | 0·0150 | 0·0329 |
| 5. 0·704 | 9·86 | 0·680 | 1·38 | 2·760 | 0·60 | 0·0571 | 0·0908 |
| 6. 0·118 | 1·75 | 0·572 | 1·88 | 0·161 | 0·22 | 0·0210 | 0·0422 |
| 7. 0·174 | 1·59 | 0·445 | 2·12 | 0·134 | 0·32 | 0·0242 | 0·0311 |

Attention is drawn to the exceptional amount of phosphoric acid in No. 5. N. H. J. M.

Testing of Various Soils as regards their Manurial Requirements. By BERNHARD SCHULZE (*Bied. Centr.*, 1901, 30, 585—586; from *Jahresber. agrik.-chem. Versuchsstat. Landw.-Kammern Prov. Schlesien*, 1899, 15).—Pot experiments were made with the following soils (1) humous loess (K₂O, 0·202; P₂O₅, 0·069; CaCO₃ and humate, 0·184 per cent.); (2) loamy sand (K₂O, 0·042; CaO, 0·519, and P₂O₅, 0·033); (3) sandy loam (K₂O, 0·062; CaO, 0·318, and P₂O₅, 0·075 per cent.); (4) loam (K₂O, 0·113; CaO, 0·319, and P₂O₅, 0·075 per cent.); (5) black loam (K₂O, 0·262; CaO, 1·193, and P₂O₅, 0·142 per cent.). Oats were grown in all the soils, and peas in (5) and (6). The yields of oats and peas obtained without manure, and with nitrogen, potassium, lime, and phosphoric acid in various mixtures, are given in tables.

As regards the wants of the different soils, the conclusion is drawn that No. (2) requires a complete manure, that (2) and (3) decidedly require phosphoric acid, and that (4) and (5) require phosphoric acid

more for peas than for oats. The amount of potassium in (4) sufficed for oats, but not for peas; (5) required potash for both crops, but especially for peas.

N. H. J. M.

Assimilation of Nitrogen and Phosphoric Acid at Three Periods of Growth. By KURT BIELER and K. ASÖ (*Bull. Coll. Agr. Tokyo Imp. Univ.* 1901, 4, 241—254).—Pot experiments with three cereals (barley, wheat, and oats), and two cruciferous plants (rape and mustard) grown in sand manured with the same amounts of double superphosphate, potassium and calcium carbonate, and ammonium sulphate. Plants were taken up for analysis after $2\frac{1}{2}$ and 4 months and after flowering. The amounts of dry produce, including roots, nitrogen, ash, and phosphoric acid were determined in each case.

It was found that the barley plants took up about the same amount of nitrogen as the same number of wheat and oat plants, and that although the amount of total ash of the barley at the end of the experiments was the greatest, the amount of phosphoric acid was the smallest. The manure applied sufficed for the complete development of the wheat and oats, but not for barley.

Rape plants were found to contain rather less nitrogen and phosphoric acid at the end of the third than at the end of the second period, although there were gains both in dry matter and ash.

Both the cereals and *Cruciferae* assimilated about the same amount of nitrogen, but the latter, especially rape, took up more phosphoric acid; of the three cereals, wheat assimilated the greatest amount of phosphoric acid.

N. H. J. M.

Examination of Hay to ascertain the Changes in the Amounts of Food Constituents, Phosphoric Acid, and Potash caused by different Manuring. By BERNHARD SCHULZE (*Bied. Centr.*, 1901, 30, 583—585; from *Jahresber. agrik.-chem. Versuchsstat. Landw.-Kammer Prov. Schlesien*).—Analyses of the hay from three meadows, each divided into several plots under different manurial treatment, showed that potassium manures, when applied alone or with lime, had the greatest effect on the yield of hay; the crop also contained the greatest amount of potassium. The yield of proteids did not always have a decided relation to the manure applied, but was highest when potassium manures were applied alone. The production of carbohydrates was, however, in direct relation to the potassium manuring. Phosphoric acid and calcium did not give any definite results, and the production of fat in the plants could not be directly connected with any manure constituent.

N. H. J. M.

Influence of the Amount of Water in the Soil, and the Manure, on the Yield and Composition of Italian Rye Grass and Clover. By CONRAD VON SEELHORST, N. GEORGS and FAHRENHOLTZ (*Bied. Centr.*, 1901, 30, 625—630; from *J. Landw.*, 1900, 48, 265. Compare Abstr., 1899, ii, 609, and this vol., ii, 274).—Clover and rye grass were grown in small plots of loamy soil without and with minerals; the grass had sodium nitrate in addition to mineral manure. There were three sets of plots: (1) with small, (2) with moderate, and

(3) with large amounts of water. The yields and composition of the produce are recorded.

It was found that an increased supply of water in the soil increased the yields of clover and its chief constituents; it also increased the yield of grass, but not, to any extent, the amount of proteids in the grass, owing to insufficient nitrogen in the soil.

The quality both of clover and grass is injured by excess of water in the soil. Both the proteid and the fat in the first cutting of clover were reduced in quantity. The percentage of ash in clover and grass increased with the amount of water in the soil. N. H. J. M.

Carob. By J. DUGAST (*Ann. Agron.*, 1901, 27, 444—445; from *J. Agr. prat.*, 1901, i, 598).—The whole fruit (1), the pods (2), and the seeds (3) of carob (*Ceratonia siliqua*) obtained from Algeria was found to have the following percentage composition:

| Water. | Nitrog. Matter. | Saccharose. | Glucose. | Starch. | Fat. | Pectic matters. | Cellulose. | Ash. |
|----------|--------------------|-------------|----------|---------|------|--------------------|------------|------|
| 1. 19.68 | 5.47 | 20.32 | 16.42 | | 0.80 | 2.88 | 7.80 | 2.53 |
| 2. 20.40 | 3.75 | 23.00 | 11.20 | — | 0.57 | 3.28 | 8.14 | 2.47 |
| 3. 14.10 | 18.56 | — | — | 56.55 | 2.64 | — | 5.33 | 3.00 |

The numbers under starch include saccharifiable cellulose.

The results show that carob is very suitable as a food for horses. It has been suggested that the fruit might be employed for the production of alcohol, and it is estimated that it would be possible to obtain 30 hectolitres of alcohol per hectare. N. H. J. M.

Pressed Grapes, compared with Hay and Straw for Cattle Food. By FLORIANO GUERRIERI (*Chem. Centr.*, 1901, ii, 737; from *Staz. sper. agrar. ital.*, 34, 338—346).—The following analyses of pressed grapes show that they are of less value than hay and straw, and can, at most, be employed as a substitute for straw:

| Water. | Starch. | Sugar. | Dextrin. | Crude fibre. | Crude fat. | Crude proteid. | N. | Ash. | | |
|-------------------|--------------------|--------|----------|----------------------------------|----------------------------------|---------------------------------|-------------------|--------------------|-------|-------------------|
| 16.72 | 14.58 | 1.57 | 3.63 | 42.53 | 0.64 | 2.89 | 0.588 | 2.905 | | |
| K ₂ O. | Na ₂ O. | CaO. | MgO. | Fe ₂ O ₃ . | Al ₂ O ₃ . | P ₂ O ₅ . | SO ₃ . | SiO ₂ . | Cl. | CO ₂ . |
| 0.25 | 0.09 | 0.78 | 0.02 | 0.38 | 0.07 | 0.17 | 0.17 | 0.21 | 0.005 | 0.21 |

N. H. J. M.

Composition and Nutritive Value of Malt Germs and the Dried Residues of Germinated Barley from Italian Breweries. By PIETRO SCARAFIA (*Chem. Centr.*, 1901, ii, 736—737; from *Staz. sper. agrar. ital.*, 34, 321—337).—The results of analyses of malt germs (1 and 2) and of residues (3) differ considerably from those given by Wolff and Settegast:

| Water. | Crude fat. | Crude proteid. | Digestible proteid. | Crude fibre. | Pentosans. | Ash. |
|----------|---------------|-------------------|------------------------|-----------------|------------|-------|
| 1. 14.10 | 3.46 | 12.08 | 6.80 | 15.24 | 11.98 | 9.63 |
| 2. 8.59 | 1.85 | 15.89 | 9.29 | 12.51 | 13.42 | 12.64 |
| 3. 9.39 | 6.44 | 17.99 | 11.49 | 17.25 | 13.66 | 7.39 |

N. H. J. M.

Influence of Variety [of Potatoes] and Manures on the Quality of the Starch. By CH. GUFFROY (*Ann. Agron.*, 1901, 27, 442—443; from *J. Agr. prat.*, 1901, i, 539).—Different varieties of potatoes produced starch grains varying widely in size. As regards the effect of manures, it was found that potassium chloride always produced starch of good quality, the grains being smaller than when the sulphate was employed. Complete manure produced the largest grains, whilst dung alone gave less satisfactory results than when employed in conjunction with phosphates. Of the different manures, phosphoric acid always had the greatest effect. N. H. J. M.

Artificial Manures and Humus. By K. DE VRIES (*Ann. Agron.*, 1901, 27, 443—444; from *Deut. landw. Presse*, 1901, 296).—The results of analyses of Groningen soils, some for a long time manured only with artificial manures and others which had received farmyard manure alone, showed that the different manuring had had no effect on the amount of humus. The fact that the soils which had only artificial manures showed no exhaustion of humus is attributed to the humification of the large crop residues. N. H. J. M.

Fermentation of Nitrogenous Substances in Farmyard Manure. By P. PIERRE DEHÉRAIN and C. DUPONT (*Ann. Agron.*, 1901, 27, 401—427).—The ferments of farmyard manure transform the nitrogen of urine, uric acid, and hippuric acid into ammonium carbonate. Hippuric acid only ferments in presence of air, whilst urea and uric acid ferment in an atmosphere of carbon dioxide. In practice, the fermentation is not rapid enough to prevent the addition of litter containing urine to manure heaps without loss of ammonia.

The proteids of farmyard manure ferment very incompletely in absence of air, and not at all in very alkaline media. Most of the nitrogen is converted into ammonium carbonate, a small quantity being liberated in the free state. Carbon dioxide, hydrogen, methane, and, frequently, hydrogen sulphide are produced. N. H. J. M.

Analytical Chemistry.

Practical Methods for the Rapid Spectroscopic Analysis of Gases. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1901, [vii], 23, 447—482).—A description of an apparatus employed in the spectroscopic examination of gases under approximately atmospheric pressure, and a table giving the wave-lengths of the prominent lines exhibited under these conditions by volatile elements and compounds.

G. T. M.

Indicators for Use with Artificial Light. By A. KUFFERATH (*Zeit. angew. Chem.*, 1901, 14, 916—918).—A series of experiments

with methyl-orange, fluorescein, cochineal, corallin, *p*-nitrophenol, alizarin-green B, resazurin, and luteol (Autenrieth, *Abstr.*, 1895, i, 572) to ascertain whether these can be successfully used in titrations when using artificial light.

The conclusion drawn is that the source of light is immaterial when using *p* nitrophenol or fluorescein, but when working with the other indicators acetylene light is preferable.

L. DE K.

Indirect Weighing of Quantitative Precipitates; Rapid and Accurate Method for Determining the Weight of a Precipitate without Separating it from the Liquid. By R. W. THATCHER (*J. Amer. Chem. Soc.*, 1901, 23, 644—668).—The author's method is briefly as follows:—The metal to be determined is converted in the usual manner into an insoluble compound. The bulk of the liquid is, if necessary, removed, and the remainder, together with the precipitate, is introduced into a pycnometer of known weight and capacity and the whole is weighed. A portion of the clear liquid is then taken off and its sp. gr. ascertained by using a smaller pycnometer. From these data and the known sp. gr. of the precipitate, the weight (x) of the same may be calculated by using the formula $x = d(a - bd')/d - d'$, in which a represents the total weight, b the total volume, d the sp. gr. of the precipitate, and d' the sp. gr. of the liquid.

Specific gravities of precipitates may be readily ascertained as follows. A known weight of, say, pure sodium chloride is precipitated with a sufficiency of silver nitrate, the precipitate is introduced in the pycnometer, which is then filled and weighed; x now being the known quantity, d may be in turn found by calculation. To find the sp. gr. of calcium oxalate, a known weight of pure calcium carbonate is dissolved and precipitated with ammonium oxalate, &c.

L. DE K.

Automatic Filter-Washer. By JAMES MARION PICKEL (*J. Amer. Chem. Soc.*, 1901, 23, 589—593).—The author has devised an automatic filter-washer which is well adapted for washing the soluble phosphates out of commercial fertilisers. A reservoir containing the liquid with which the washing is to be effected is connected by a rubber tube provided with two clamps to the delivery vessel; by means of these clamps the rate of flow can be regulated. In the interior of the delivery vessel is a small intermittent siphon which delivers the liquid on to an inverted funnel covering the substance to be washed; this funnel is of such a size as to nearly cover the filter-paper contained in a larger funnel.

E. G.

Analysis of Gases by means of the Electric Spark. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1901, [vii], 23, 433—447).—Pure oxygen, when contained over mercury and submitted to the action of the electric spark, yields a small amount of ozone, which superficially oxidises the mercury; a mixture of oxygen and nitrogen gives rise to nitrogen peroxide, the product giving a characteristic pink coloration with ferrous sulphate and concentrated sulphuric acid. Hydrogen is not affected by the electric discharge and this agent does not readily promote its combination with nitrogen to form ammonia. Nitrogen under these

conditions reacts with acetylene or ethylene, giving rise to hydrogen cyanide (compare Abstr., 1897, i, 330). Argon and helium, when mixed with benzene vapour and sparked in the presence of mercury, exhibit respectively their characteristic green and orange-coloured luminescent spectra. Nitrogen monoxide and trioxide, when sparked for some time, yield a mixture of nitrous fumes, oxygen, and nitrogen. The oxides of chlorine detonate under the influence of the electric spark, yielding their constituent elements. Sulphur dioxide is partially decomposed into the trioxide and free sulphur; carbon dioxide after prolonged action yields an appreciable amount of carbon monoxide and oxygen. Carbon monoxide, under similar conditions, yields a mixture of carbon and the dioxide. The hydrides of chlorine, bromine, and iodine are partially decomposed under the influence of the electric spark, whereas hydrogen fluoride is not affected. Water, and the hydrides of sulphur, selenium, and tellurium, undergo a similar decomposition; in all these cases, the action becomes more complete as the atomic weight of the non-metal increases. Ammonia and phosphine are completely decomposed after 2 hours' exposure to the electric discharge; arsine, stibine, and hydrogen silicide are also rapidly resolved into their elements. The hydrocarbons also undergo decomposition, acetylene being in each case an intermediate product; this substance subsequently gives rise to hydrogen and carbon, a limit to this reaction being attained when the volumes of the hydrogen and unaltered hydrocarbon are in the ratio 7:1. Compounds containing carbon, hydrogen, and oxygen decompose under these conditions, yielding acetylene, water, and the oxides of carbon.

Carbon oxysulphide gives rise to carbon monoxide and sulphur, whilst carbon disulphide is resolved into its elements. The mercaptans and thio-ethers are decomposed, yielding hydrogen sulphide, acetylene, hydrogen, sulphur, and carbon.

The alkyl chlorides furnish hydrogen chloride, the corresponding bromides give rise to hydrogen bromide, and the iodides to iodine; in addition to these products, the alkyl haloids yield acetylene, carbon, and hydrogen. Phosphorus trifluoride is resolved into phosphorus and the pentafluoride; the latter compound is not altered by the electrical discharge and in this respect resembles boron chloride and the fluorides of boron, silicon, and sulphur. Cyanogen and cyanogen chloride are resolved into their elements. Hydrogen cyanide is partially dissociated into acetylene and nitrogen. Methylamine and its analogues yield hydrogen cyanide, acetylene, carbon, and hydrogen. G. T. M.

Estimation of Solution of Hydrogen Peroxide. By WILLIAM A. H. NAYLOR and C. S. DYER (*Pharm. J.*, 1901, [iv], 13, 131—132).—The gasometric method of estimating solutions of hydrogen peroxide by means of potassium permanganate and sulphuric acid in a nitrometer charged with brine is rendered inaccurate by the evolution of chlorine, which is incompletely absorbed by the water; the results furnished by this process are considerably higher than those obtained by collecting the oxygen over mercury, but if a saturated solution of magnesium sulphate is substituted for the brine, the results agree with those obtained when mercury is used. In any case, however, the

permanganate method yields somewhat higher results than that of Mason (*Chemist and Druggist*, 1881, 56), which involves the use of potassium dichromate and gives concordant results whether the oxygen is collected over brine, saturated solution of magnesium sulphate, or mercury. E. G.

Estimation of Chlorate in Electrolytic Bleaching Solutions and Potassium Chlorate Lyes. By HUGO DITZ (*Chem. Zeit.*, 1901, 25, 727—728).—A slight modification of the former apparatus (Abstr., 1900, ii, 241). It is now also stated that the reaction between potassium chlorate, potassium bromide, and hydrochloric acid is complete within five minutes; potassium iodide is then decomposed by the liberated bromine and the free iodine titrated. L. DE K.

Estimation of Sulphur in Iron and Steel. By WILLIAM A. NOYES and L. LESLIE HELMER (*J. Amer. Chem. Soc.*, 1901, 23, 675—679).—Five grams of the finely divided sample are dissolved in 200 c.c. of water and 8 c.c. of bromine, and filtered off from any insoluble matter, which must afterwards be tested for sulphur by fusion with oxidising mixture in the usual manner, or 5 grams of the sample are mixed with 7 grams of potassium chlorate and gradually added to 120 c.c. of nitric acid of sp. gr. 1.2 containing 1 gram of potassium bromide; the whole is then evaporated to dryness, and the residue dissolved in hydrochloric acid, when any insoluble matter must also be examined for sulphur. Care should be taken to avoid contact with sulphurous fumes from the illuminating gas.

In either case, the iron solution is poured into 130 c.c. of 10 per cent. ammonia, and the whole diluted to 500 c.c. and filtered through a dry filter. Three hundred c.c. of the filtrate are evaporated to 100 c.c., one drop of hydrochloric acid of sp. gr. 1.12 is added, and the sulphuric acid precipitated as usual by means of barium chloride. The test experiments prove the great accuracy of the method. L. DE K.

Estimation of Sulphur in Oils. By FERDINAND JEAN (*Ann. Chim. anal. appl.*, 1901, 6, 321).—So-called cooling oils contain a small quantity of added sulphur, sometimes to the extent of 0.7 per cent. The author estimates this as follows: 5 grams of the sample are heated at about 150° in an enamelled dish, and saponified by adding 4 c.c. of aqueous sodium hydroxide of sp. gr. 1.33 and 2 c.c. of alcohol; the whole is evaporated to dryness with constant stirring. The mass is dissolved in hot water and the soap separated by saturating the liquid with salt; the precipitate is then washed with brine. The filtrate is mixed with an excess of seltzer water, and the sulphide titrated with *N*/10 iodine, using starch as indicator.

Treated in this manner, a sample of colza oil gave 0.031, and one of rapeseed oil, 0.044 per cent. of sulphur. L. DE K.

Gravimetric Estimation of Tellurium. By ALEXANDER GUTHRIE (*Ber.*, 1901, 34, 2724—2726).—In the gravimetric estimation of tellurium by reduction to the metal, hydrazine hydrate or hydrochloride may be employed with great advantage, as the reduction can be carried out in neutral solution, and the reoxidation of the tellurium to telluric

acid is largely avoided. Five analyses of telluric acid by this method showed a maximum error of 0.2 per cent. and two analyses of the dioxide gave values within 0.1 per cent. of the calculated percentage of tellurium.

T. M. L.

[Estimation of Nitrogen] in Urine for Clinical Purposes. By ADOLF JOLLES (*Chem. Centr.*, 1901, ii, 663—664; from *Centr. inn. Med.*, 1901, 22, 719—723).—Five c.c. of urine are mixed with 5 c.c. of water, and 5 c.c. of this are diluted to 150 c.c. and heated with 2 c.c. of sulphuric acid. A solution containing 4 grams of potassium permanganate per litre is now added 1 c.c. at the time, until after 15 minutes' boiling the colour is no longer discharged. By this means, the various minor nitrogenous constituents of urine, uric acid, purine bases, hippuric acid, oxaluric acid, proteids, carboxylic acids, and allantoin furnish products which, like urea and ammonia, yield the whole of their nitrogen as gas when treated with bromine in the presence of sodium hydroxide. The liquid is decolorised by adding a little oxalic acid, made alkaline with sodium hydroxide, and the nitrogen then liberated in the author's azotometer (*Abstr.*, 1900, ii, 450).

L. DE K.

Estimation of Ammonia in Animal Liquids and Tissues. By MARCELLUS NENCKI and J. ZALESKI (*Zeit. physiol. Chem.*, 1901, 33, 193—209).—The percentages of ammonia obtained by the method previously described (*Abstr.*, 1897, ii, 343) vary with the proportions of blood and lime-water employed; the authors now recommend the distillation of the blood itself diluted with water, as it contains sufficient alkali to decompose all ammonium salts present. Good results are also obtained when magnesia is employed in place of lime-water; the addition of magnesia has the advantage that it prevents frothing and an excess does not affect the result. The distillation is carried out at a temperature of 30° under reduced pressure, and it is necessary to continue the operation until two-thirds of the liquid has passed over. The distillation is facilitated by introducing a vertical condenser and receiver between the vessel which contains the acid and the pump. With animal tissues, it is necessary to macerate thoroughly by grinding with fine sand, before the distillation is carried out.

The amounts of oxygen absorbed when alkaline solutions of the following proteids—serum-albumin, serum-globulin, and oxyhæmoglobin from horses' blood—are exposed to the atmosphere have been determined by the method previously described (Nencki and Sieber, *J. pr. Chem.*, 1882, [ii], 26, 6).

J. J. S.

Rapid Estimation of Nitrates in Soils. By CARLO MONTANARI (*Chem. Centr.*, 1901, ii, 793—794; from *Staz. sperim. agrar. ital.*, 1901, 34, 690—693).—The author applies Grandval and Lajoux's method for estimating nitric acid in water or air to soils. Ten to 20 grams of the carefully selected sample are mixed with 100 c.c. of water and frequently shaken for some hours. Fifty c.c. of the filtrate are then shaken with 1—2 grams of purified animal charcoal and filtered, 10 or 20 c.c. of the filtrate are evaporated to dryness on the water-bath, and treated in the cold with a reagent made by dissolving 3 grams of crystallised phenol in 37 grams of sulphuric acid. After adding some water and supersaturating with ammonia, the liquid is diluted to 100, 250, 500, or

more c.c., and the colour is then compared with a solution obtained in a similar way from a known quantity of potassium nitrate.

L. DE K.

Estimation of Phosphorus and Sulphur in Acetylene and other Combustible Gases. By PAUL EITNER and GUSTAV KEPPELER (*Chem. Centr.*, 1901, ii, 662; from *J. Gasbel.*, 1901, 44, 548—552).—The gas is collected over brine in a gasometer and then burnt in a blowpipe burner supplied with oxygen. By means of an arrangement similar to that employed in the estimation of sulphur in illuminating gas, the products of combustion are drawn through two ten-bulb tubes containing water and an alkaline solution of bromine and connected with an empty Volhard tube. The phosphoric and sulphuric acids are then estimated as usual; a portion of the former deposits on the sides of the apparatus before it reaches the absorbing tubes and must be estimated separately.

L. DE K.

Simplification of Meineke-Woy's Method of Estimating Phosphoric Acid as Phosphomolybdic Oxide; Precipitation of pure Ammonium Phosphomolybdate by Molybdate Solution containing Citric Acid; Conversion of Wagner's Molybdate Magnesia Process into a purely Molybdate one. By ANTON SEYDA (*Chem. Zeit.*, 1901, 25, 759—768).—The author has found by a series of experiments that the most accurate way of estimating phosphoric acid, including citrate-soluble acid, is its conversion into phosphomolybdic oxide.

The only possible objection to the process is the probable precipitation of free molybdic acid, particularly in the presence of a large excess of molybdate solution. This is, however, rarely the case when precipitating in the cold and using a stirring apparatus for 15 minutes. If no citric acid is already present, an addition of 2 grams of it will prevent the precipitation of molybdic acid. Solutions containing no iron may be heated to 30°, but those containing it, not higher than 20°; in this case, the liquid should be filtered 15 minutes after it ceases to be stirred. If the presence of free molybdic acid is suspected, the precipitate should be redissolved in dilute ammonia, mixed with 50—100 c.c. of dilute molybdate solution, and precipitated hot with nitric acid; this operation may sometimes require repeating. (For the exact strength and proportions of the reagents, the original paper should be consulted.) The liquid may be filtered while still hot and the precipitate washed with a hot solution containing 5 per cent. of ammonium nitrate and 1 per cent. of nitric acid. Alcohol of 95 per cent. should be used to rinse the precipitate from the sides of the porcelain Gooch crucible. The conversion of the precipitate into the oxide is only complete when it has a uniform appearance throughout its mass.

L. DE K.

Estimation of Phosphates in Potable Waters. By CHARLES LEPIERRE (*Bull. Soc. Chim.*, 1901, [iii], 25, 800).—The method described by Woodman and Cayvan (this vol., ii, 344) for the estimation of phosphates in potable waters is identical with that previously published by the author (*Abstr.*, 1898, ii, 47).

N. L.

Arsenic in Coal and Coke. By ALFRED C. CHAPMAN (*Analyst*, 1901, 26, 253—256).—A large quantity of the sample is finely powdered and well mixed; 0.5—2 grams are then carefully mixed with 2 grams of magnesium oxide and 0.5 gram of anhydrous sodium carbonate and introduced into a deep silver crucible. This is supported in a slanting position and heated by a flame so as to keep the bottom at a dull red heat, the contents being occasionally stirred by means of a platinum wire. After about one hour, the oxidation is complete, but to make sure 0.5 gram of ammonium nitrate is added and a stronger heat applied for five minutes. When cold, the contents are transferred to a beaker, dissolved in dilute sulphuric acid, and heated to expel any nitric acid. This solution is then quantitatively tested for arsenic in the Marsh-Berzelius apparatus, the mirrors obtained being compared with standards.

Tables are given showing the amount of arsenic found in coal, in the coke obtained therefrom, and also in the ashes. A small proportion of the arsenic is retained in the ash as ferric arsenate or calcium arsenate.

L. DE K.

Method for the Destruction of Organic Matter applicable to the Detection of Inorganic Poisons, more especially Arsenic and Antimony. By GEORGES DENIGES (*J. Pharm. Chim.*, 1901, [vi], 14, 241—246).—The organic matter is destroyed, first by treatment with concentrated nitric acid and potassium permanganate and finally with concentrated sulphuric and nitric acids. The method is rapid, and of general application to all toxicological analyses for inorganic poisons.

H. R. LE S.

Estimation of Boric Acid. By G. CARNIELLI (*Gazzetta*, 1901, 31, i, 544—553).—The author has examined the various methods which have been proposed for the estimation of boric acid and draws the following conclusions from his results.

The Berzelius-Stromeyer process of precipitation as potassium fluoborate is untrustworthy, especially when used for sodium compounds of boric acid.

The Rosenbladt-Gooch method, depending on the ready volatility of ethyl borate, gives moderately concordant results when carefully carried out and when all the precautions suggested by Moissan (*Abstr.*, 1893, ii, 435) are taken.

Smith's plan (*Chem. News*, 1882, 46, 286) of precipitating boric acid by means of manganous sulphate and determining the excess of the latter by titration with permanganate, gives good results when carried out according to the present author's modification, which is as follows. Ten c.c. of a 4 per cent. borax solution are mixed with 20 c.c. of a 0.6 per cent. manganous sulphate solution and 30 c.c. of strong alcohol, the liquid being left in a covered beaker for half an hour and then filtered, the precipitate being washed with strong alcohol to remove all the manganous sulphate. The total filtrate is then evaporated to dryness on a water-bath, the residue dissolved in water, and the solution mixed with 7 c.c. of an 80 per cent. zinc sulphate solution and faintly acidified; the liquid is then heated to boiling, poured into a measuring flask to which is also added a strong excess of standard permanganate

solution. After making up to volume with distilled water, aliquot parts of the solution are titrated with decinormal oxalic acid to determine the excess of permanganate.

Thomson's volumetric method (Abstr., 1894, ii, 28), in which the boric acid is set free and then titrated with standard alkali solution in presence of glycerol, using phenolphthalein as indicator, is rapid and accurate.

The spectroscopic method proposed by Föhr (*Zeit. anal. Chem.* 1887, 26, 79) gives good results, but not for very small quantities of boric acid.

T. H. P.

Estimation of Carbon in Steel and Iron. By SCHMITZ (*Chem. Zeit.*, 1901, 25, 684—685).—The steel borings are dissolved as usual in a mixture of dilute sulphuric acid, chromic acid, and copper sulphate in a special flask and the gases evolved are passed by means of a current of air over platinum spirals heated to redness. The carbon dioxide after being dried is then absorbed in the usual manner by soda-lime.

L. DE K.

Oxidation of Organic Nitrogen Compounds and the Estimation of the Carbon and Nitrogen therein by the Moist Process. By MISS E. VAN AKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 91—95).—Using Fritsch's method (Abstr., 1897, ii, 124) of simultaneously estimating carbon and nitrogen in organic substances, the author finds that carbamide, dimethyl- and tetramethyl-carbamide, acetylcarbamide, and thiocarbamide yield only half their nitrogen as ammonia.

Cyclic nitrogen compounds, such as alloxan and malonureide, behave similarly; with uric acid and caffeine, the deficit is not so large. Oxamide, although giving more than half its nitrogen as ammonia, exhibits a much larger deficit than malonamide, succinamide, or asparagine. Fritsch appears to be incorrect in stating that his process is applicable to all nitrogen compounds which can be analysed by Kjeldahl's method.

K. J. P. O.

[Analysis of Mixtures of Carbon Oxysulphide, Hydrogen Sulphide, and Carbon Dioxide.] By WALTHER HEMPEL (*Zeit. angew. Chem.*, 1901, 14, 865—868).—See this vol., ii, 651.

Estimation of Free Alkali in the Presence of Carbonate. By W. E. RIDENOUR (*Chem. Centr.*, 1901, ii, 741; from *J. Franklin Inst.*, 1901, 152, 119—121).—According to Thompson, the liquid is first titrated with *N*-hydrochloric acid, using phenolphthalein as indicator; this gives the free alkali and half of the carbonate. After adding methyl-orange, the titration is continued, and the other half of the carbonate is thus estimated. The author has found that this is not strictly correct, and that the process may be improved by means of the following correction. To obtain the number of c.c. of *N*-hydrochloric acid which correspond with the carbonate contained in the mixture, the result of the methyl-orange titration should be multiplied by 2 and divided by the factor 104.5726.

L. DE K.

Precipitation and Separation of Silver by Electrolysis.

By W. H. FULWEILER and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1901, 23, 582—585).—By the electrolytic method, silver can be completely separated from copper, from copper and cadmium if the electrolyte is heated at 75—80° before passing the current, and also from cadmium, zinc, and nickel. E. G.

Estimation of Calcium, Strontium, and Barium as the Oxalates. By CHARLES A. PETERS (*Amer. J. Sci.*, 1901, [iv], 12, 216—224).—Calcium oxalate is completely precipitated from a solution containing an excess of ammonium oxalate, but the precipitate must not be washed too much, as it is appreciably soluble in pure water. Strontium oxalate is completely precipitated by ammonium oxalate from a solution containing 1/5 of its volume of 85 per cent. alcohol. The precipitation of barium oxalate is complete if the solution contains 1/3 of its volume of 85 per cent. alcohol.

Calcium, strontium, and barium oxalates, after decomposition with hydrochloric acid, may be accurately titrated with permanganate if some manganous salt be added.

Strontium and barium oxalates (like calcium oxalate) are converted into carbonates by ignition, and may be weighed in this form.

J. McC.

Simple Reaction for distinguishing Aragonite and Calcite.

By W. MEIGEN (*Centr. Min.*, 1901, 577—578).—The finely powdered mineral is placed in a dilute solution of cobalt nitrate and this boiled for a few minutes. In the presence of aragonite, there is a lilac-red precipitate of basic cobalt carbonate, whilst calcite remains white, or, in the presence of organic matter, becomes yellowish. Barium and strontium, but not magnesium, carbonates give the same result as aragonite, and calcium phosphate produces a blue precipitate. This reaction is made use of for the purpose of distinguishing calcite and aragonite in various animal and vegetable secretions of calcium carbonate.

L. J. S.

Volumetric Estimation of Lead Dioxide in Red Lead. By MAX LIEBIG (*Zeit. angew. Chem.*, 1901, 14, 828).—0.5 gram of the sample is rinsed with a little water into a small Erlenmeyer flask and 25 c.c. of *N*/10 sodium thiosulphate are added. Ten c.c. of acetic acid (containing not more than 40 per cent. of real acid) are now added in order to dissolve the substance. After introducing 10 c.c. of a solution of potassium iodide (1:10) and starch solution as indicator, the excess of thiosulphate is titrated with *N*/10 iodine. The end reaction is noticed by the bright yellow lead iodide becoming discoloured. The number of c.c. of iodine consumed multiplied by 239 represents the percentage of lead dioxide in the red lead.

L. DE K.

Electrolytic Separation of Mercury from Copper. By C. ROSCOE SPARE and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1901, 23, 579—582).—In reply to the statement of Emil Goecke (*Inaug. Diss.*) that the separation of mercury from copper cannot be satisfactorily effected electrolytically, the authors publish the results of a number of estimations to prove the accuracy of the method; unlike

Goecke, they find that the deposit of mercury is free from copper. They also obtained satisfactory results in the presence of copper, cadmium, and zinc. E. G.

Comparison of the Quantitative Action of Reducing Agents on Mercury and Bismuth Salts. By THOMAS TYRER and CHAS. T. TYRER (*Pharm. J.*, 1901, [iv], 13, 144).—A comparison of a modification of the method for the estimation of mercury by reduction with hypophosphorous acid described by Bennett (this vol., ii, 131) with other reduction methods.

Stannous chloride gives low results owing to the loss occasioned by the fine state of division of the mercury. With formaldehyde in alkaline solution, the same difficulty occurs, whilst in acid solution the reduction is incomplete. Phenylhydrazine in alkaline solution produces only partial precipitation, and in acid solution no reduction takes place. With sodium arsenite in acid solution, reduction is slow and incomplete, but in presence of an alkali, complete reduction occurs; the results, however, are somewhat lower than those obtained by the hypophosphorous acid method. A strongly alkaline solution of potassium antimony tartrate effects complete reduction, but the product is contaminated with traces of an antimony salt. By boiling solutions of mercury salts with phosphorous acid in large excess, fair results are obtained. A modification of the method of Vanino and Treubert (*Abstr.*, 1897, ii, 601), in which hypophosphorous acid is used in presence of hydrogen peroxide, is also found to be satisfactory.

Estimations of bismuth salts were made with hypophosphorous acid and with formaldehyde, but although good results were obtained, neither process has any advantage over the sulphide method.

E. G.

Estimation of Metallic Iron in reduced Iron. By ALBERT MARQUARDT (*Chem. Zeit.*, 1901, 25, 743—744).—A modification of the process laid down in the German Pharmacopœia. 0.3 gram of the reduced iron is introduced into a glass-stoppered 25 c.c. flask and a solution of 1 gram of potassium iodide in 4 c.c. of water is added, together with 1.5 gram of pure iodine. The mixture is allowed to stand for an hour, being thoroughly shaken every 10 minutes. The solution is then diluted to 100 c.c. and the excess of iodine titrated according to the earlier directions.

L. DE K.

Formation of Carbon during the Electrolysis of Ammonium Oxalate. By HANS VERWER (*Chem. Zeit.*, 1901, 25, 792—793).—Avery and Dales (*Abstr.*, 1899, ii, 814) have stated that iron deposited by electrolysis from a solution containing ammonium oxalate contains carbon. The author finds that such is the fact, particularly when a high tension current is used. In any case, however, no separation of carbon takes place until the greater portion of the iron has been deposited. It also appears that carbon is not deposited directly from the oxalate, but from the ammonium carbonate or ammonium hydrogen carbonate, which results from the electrolytic decomposition of the oxalate. On dissolving the iron, an odour of hydrocarbons is noticed, showing that the carbon, partially at least, is in a state of combination with the iron.

L. DE K.

Reduction of Ferric Salts. By GILBERT T. MORGAN (*Analyst*, 1901, 26, 225—227).—Instead of using granulated zinc for the reduction of ferric salts, the author prefers a zinc-copper couple, produced by immersing 8 grams of granulated zinc in 200 c.c. of a 10 per cent. solution of copper sulphate. The reduction is complete after 10 minutes, and the liquid may be decanted from the zinc and, if necessary, passed through a filter. No iron is precipitated and retained by the undissolved zinc. L. DE K.

Potassium Thiocyanate as Indicator when Reducing Ferric Salts. By LUCIEN L. DE KONINCK (*Chem. Centr.*, 1901, ii, 661; from *Bull. Assoc. belge Chim.*, 1901, 15, 230).—Ebeling's proposal to add potassium thiocyanate when a ferric solution is being reduced with zinc (this vol., ii, 424, 480) is not to be recommended. Potassium thiocyanate is reduced by zinc, and any portion which has escaped reduction is readily oxidised by permanganate. L. DE K.

Qualitative Detection of Small Quantities of Nickel in the Presence of Cobalt. By HUGO DITZ (*Zeit. angew. Chem.*, 1901, 14, 894—897).—The solution, which should be neutral, is mixed with potassium chromate in slight excess, and heated in a spacious flask to boiling. Five to 10 grams of potassium sodium tartrate are now added, and the boiling continued for several minutes. After cooling for some time and adding a little more water, should the colour be too strong, the liquid is examined for any brown deposit of nickel chromate. This deposit is, however, not quite free from cobalt, so the method is, as yet, only of qualitative interest. L. DE K.

Rapid Method for the Evaluation of Chromic Acid and Soluble Chromates. By LYMAN F. KEBLER (*Chem. Centr.*, 1901, ii, 708—709; from *Amer. J. Pharm.*, 1901, 73, 395—397).—One gram of the sample is dissolved in water to 100 c.c., 20 c.c. are put into a porcelain basin containing 75 c.c. of water and 2 grams of potassium iodide, and 15 c.c. of 10 per cent. sulphuric acid are added. The liberated iodine is then titrated as usual with *N*/10 sodium thiosulphate, 1 c.c. of which represents 0.003329 gram of chromium trioxide, or 0.004896 gram of potassium dichromate. The author has met with two samples of chromic acid containing a large proportion of sodium hydrogen sulphate. L. DE K.

Electrolytic Estimation of Molybdenum. By LILY G. KOLLOCK and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1901, 23, 669—671).—Molybdenum may be accurately determined in the mineral molybdenite by fusing the latter with alkali nitrate and carbonate. The fused mass is extracted with water, the filtrate acidified with sulphuric acid, and the liquid submitted to electrolysis, using a current of 0.1 ampere and 4 volts, the temperature being 75°. When precipitation is complete, the hydrated sesquioxide deposit after being washed is dissolved in dilute nitric acid, the solution evaporated to dryness, and the residue gently heated to remove the last traces of nitric acid, and then weighed as molybdic acid; if any blue spots are visible, these should be moistened with nitric acid and the drying

repeated. If it be desired to estimate the sulphur also, acetic acid may be substituted for sulphuric acid; the electrolysis then, however, occupies a longer time.
L. DE K.

Electrolytic Estimation of Uranium. By LILY G. KOLLOCK and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1901, 23, 607—609).—Uranium can be accurately estimated in solutions of the acetate, sulphate, or nitrate by the electrolytic method. If iron, chromium, nickel, or cobalt is present, the method fails, but uranium can be completely separated from barium, calcium, magnesium, or zinc in solutions of their acetates.
E. G.

Precipitation of Tin from its Sulpho-salts and its Separation from Antimony by Electrolysis. By HERMANN OST and W. KLAPPROTH (*Zeit. angew. Chem.*, 1901, 14, 817—827).—The authors have continued their researches on the electrolytic deposition of tin and antimony, using a cell with a diaphragm (*Abstr.*, 1900, ii, 692), and communicate the results in eight tables. Several illustrations are also given, one being of a modification of the former apparatus.

The separation of tin and antimony is finally recommended to be carried out as follows:—The mixed sulphides, obtained in due course, and containing at most 0.5 gram of total metal, are dissolved in as little sodium sulphide as possible and the solution is diluted to a definite bulk. In one-half of the liquid the antimony alone is estimated by adding 8 grams of sodium sulphide and water up to 80—96 c.c., and using a current of 0.1—0.2 ampere in the cold for 7 hours.

In the other portion, both tin and antimony are precipitated by adding sufficient ammonium sulphate to convert all the sodium sulphide into the ammonium compound. In addition, 40 grams of sodium sulphate are added, also 10 c.c. (= 2 grams) of ammonium sulphide. After diluting to 80—90 c.c., the liquid is electrolysed by a current of 0.3—0.5 ampere. After two hours, the precipitation is generally complete. The cathode with the sulphur precipitate is then taken from the first cell, placed in another cell containing 25 grams of sodium sulphate in 125 c.c., and a current of 0.5—1 ampere continued for an additional half-hour.
L. DE K.

Estimation of Platinum and Iridium in Platinum Ore. By ÉMILE LEIDIÉ and QUENNESSEN (*Bull. Soc. Chim.*, 1901, [iii], 25, 840—842).—The method devised by Leidié (this vol., ii, 62) for the separation of the platinum metals may be simplified when the estimation of platinum or its commercial extraction only is required. The ore is treated with aqua regia and the solution evaporated to dryness, the residue dissolved in water, treated with sodium nitrite and carbonate to remove iron, lead, &c., and distilled in a current of chlorine to remove osmium and ruthenium. The liquid is then neutralised by hydrochloric acid, and the rhodium and iridium precipitated by means of sodium nitrite and potassium chloride. The platinum and palladium nitrites remaining in solution are converted into chlorides by evaporation with hydrochloric acid, and the metals precipitated by heating with formaldehyde in alkaline solution, heated in hydrogen, dissolved in aqua regia, the palladium chloride reduced by

nitric oxide, and the platinum precipitated by ammonium chloride. Iridium is best estimated in another portion of the liquid from which osmium and ruthenium have been removed in the manner previously described (*loc. cit.*). N. L.

Estimation of the Dissolved Gases in Natural Waters. By LUDWIG W. WINKLER (*Zeit. anal. Chem.*, 1901, 40, 523—533).—The total carbon dioxide is estimated as follows: In a 250 c.c. flask with a neck 5—6 mm. in diameter, and with a piece of black caoutchouc tube slipped over the neck, 50 c.c. of dilute hydrochloric acid are boiled until all air is expelled. The caoutchouc tube is closed with a clamp, and the exhausted flask cooled and weighed. The neck is then connected with a bent tube dipping into the water to be examined, and on opening the clamp a quantity of the water is drawn into the flask. The amount is found by reweighing the flask; a delivery tube is adjusted and the carbon dioxide is boiled out, collected over mercury, and measured. To ascertain how much of it is in combination with bases, the water is titrated with $N/10$ acid and methyl-orange.

Dissolved oxygen and nitrogen may be expelled from a natural water by filling completely with the water a 500 c.c. flask, at the bottom of which lies 10 grams of calcite (in fragments free from dust) and adding 20 c.c. of hydrochloric acid (sp. gr. 1.19). If this is done skilfully, a rubber stopper carrying an evolution tube can be adjusted before any gas is evolved. The oxygen and nitrogen are completely expelled in 15—20 minutes. The gases are collected in a burette over sodium hydroxide solution, and measured after replacing this with pure water. The oxygen is then absorbed by alkaline pyrogallol introduced through the stopcock of the burette. M. J. S.

Neutral-red as a means of detecting *Bacillus Coli* in Water. By R. H. MARGILL (*J. Hyg.*, 1901, 1, 430—436).—The neutral-red test is rapid and delicate. A negative result may be taken as evidence of the absence of *Bacillus coli*. A positive result is always obtained if the *B. coli* is present, but it is advisable in such cases to use confirmatory tests. The reaction may even be employed as a rough quantitative method. W. D. H.

Neutral-red in the Bacteriological Examination of Water. By WILLIAM G. SAVAGE (*J. Hyg.*, 1901, 1, 437—450).—The neutral-red test is of great value in the routine examination of water. Although a positive result is not absolutely diagnostic of the presence of *Bacillus coli*, it is very nearly so. W. D. H.

Comparison of the Solubility of Acetylene and Ethylene. By SAMUEL A. TUCKER and HERBERT R. MOODY (*J. Amer. Chem. Soc.*, 1901, 23, 671—674).—In order to find a reagent which will absorb acetylene and leave ethylene undissolved, ammoniacal cuprous chloride was first tried, but was found to be useless for the purpose since it readily dissolves ethylene, although the gas is very slightly soluble in water or solution of ammonia. Both acetylene and ethylene are soluble in alcohol or acetone. Fuming sulphuric acid does not effect a separation, since acetylene is absorbed by it to a considerable extent. Finally, it was found that solution of ammonio-chloride of silver is an

excellent solvent for acetylene, whilst ethylene is almost insoluble in it. E. G.

Testing Marc and Plum Brandies. By ALEXANDER ZEGA (*Chem. Zeit.*, 1901, 25, 793—794).—The analysis is restricted to the estimation of the free and combined acidity (expressed as potassium hydroxide) alcohol, extract and ash, fusel oil and the testing for aldehyde, furaldehyde, and in the case of plum brandy for hydrocyanic acid. An important factor is the behaviour of the distillate towards $N/100$ potassium permanganate.

The free and total acidity are taken in the usual manner and the combined acidity is found by difference. In one instance, 100 c.c. of the sample required 0.0672 gram of potassium hydroxide to neutralise the free acid, and 0.0266 gram for the combined acid. When testing diluted commercial alcohol, it will be found that it is the combined acid which exceeds the free. The following proportion between combined and total acidity has been observed. In the case of marc brandy it varies from 1 : 1.25 minimum to 1 : 5.2 maximum; for plum brandy from 1 : 4 to 1 : 8.4; for diluted alcohol from 1 : 1.3 to 1 : 1.75.

If 1 c.c. of $N/100$ permanganate is added to 1 c.c. of the distillate contained in a 50 c.c. stoppered cylinder, it will be noticed that the brandies are more quickly oxidised than the spirit. When the mixture has turned yellowish-brown, the marc brandy and the spirit both smell of aldehyde, whilst the plum brandy has the characteristic odour of plum stones. On adding another c.c. of permanganate and waiting until the mixture has again turned yellow, the marc brandy smells of ethyl heptoate, the plum brandy has retained its odour, and the spirit has nearly lost its aldehydic odour and smells faintly of acetic acid. L. DE K.

Characteristic Reaction of Phenol. By MANSEAU (*Rev. Intern. Falsific.*, 1901, 14, 96—97).—If to an alcoholic solution of phenol is added a little ammonia and then an alcoholic solution of iodine, the latter is at first very quickly absorbed, then somewhat more slowly, and finally the liquid turns a permanent bright green, even when heated, or acidified with hydrochloric acid. Nitric or sulphuric acids destroy the colour. If an aqueous solution of phenol is to be tested, it must be mixed with an equal volume of alcohol.

None of the other phenols, such as thymol, resorcinol, naphthol, catechol, quinol, pyrogallol, creosote, or guaiacol, gives the green colour. On adding ammonia to their alcoholic solutions, catechol turns reddish-brown, quinol saffron-yellow, pyrogallol blackish-brown, resorcinol gooseberry-red changing to violet, the others are not affected. On now adding iodine, creosote turns greenish-brown; thymol flesh-red, changing on adding excess of iodine to brick-red; resorcinol assumes a colour of old brandy; naphthol turns lemon-yellow, yielding on addition of more iodine a precipitate similarly coloured. Catechol turns catechu colour without formation of a precipitate; pyrogallol turns completely black; quinol turns reddish-black; resorcinol does not change. Guaiacol behaves like creosote, and salicylic acid, although first turning yellowish-green, changes to brown and yields a precipitate. L. DE K.

Estimation of Phenol when mixed with Resinous Substances. By JOHN C. THRESH (*Pharm. J.*, 1901, [iv], 13, 138).—In "carbolised gauze," largely used in surgery, the phenol is "fixed" on the gauze by aid of resin. The amount of phenol may be estimated as follows. The gauze is placed in a flask, dilute hydrochloric acid and a few fragments of granulated zinc are added, the flask is heated, and the phenol estimated in the distillate by means of bromine.

E. G.

Titration of Phenol, Salicylic Acid, and Salol in Surgical Dressings. By FERNAND TELLE (*J. Pharm. Chim.*, 1901, [vi], 14, 289—291. Compare this vol., ii, 357).—Two grams of the finely cut cotton or gauze dressing are digested with alcohol (95°) and 2 c.c. of aqueous sodium hydroxide; 40—50 c.c. of water are then added and the liquid boiled for a few minutes. It is next diluted with water to 200 c.c., and 1.5 c.c. more added to allow for the volume occupied by the gauze or cotton. The liquid is filtered and the filtrate titrated as described in the former communication.

H. R. LE S.

Influence of Foreign Substances on Trommer's Sugar Test. By A. CIPOLLINA (*Chem. Centr.*, 1901, 25, 709—710; from *Deut. med. Woch.*, 1901, 27, 440—442).—The yellow precipitate or coloration often noticed when testing for dextrose with copper sulphate and aqueous sodium hydroxide is not necessarily due to the presence of creatinine, as it may be also caused by a 4 per cent. solution of sarcolactic acid, a 1 per cent. solution of allantoin, a 2 per cent. solution of lactic acid or asparagine, or a strong solution of isobutyric acid, benzoic acid, or thymol. The presence of an equal bulk of alcohol has also the same effect. With the exception of creatinine, these substances only interfere when present in large quantities, and on adding more alkali the yellow colour changes to red. The "yellow Trommer reaction" is therefore a characteristic test for creatinine.

Creatine behaves indifferently. A 0.1 per cent. solution of guanidine carbonate in a 1 per cent. solution of sugar (? dextrose) also gives the yellow reaction if excess of alkali be avoided; a 0.1 per cent. solution of glycocyamine also gives the reaction; weaker solutions do not. Glycocyamidine behaves like glycocyamine.

L. DE K.

Estimation of Lactose in Milk. By C. RIEGLER (*Ann. Sci. Univ. Jassy*, 1901, 1, 321—325).—The proteid matter is first removed by treating 10 c.c. of the milk with an equal volume of a 4 per cent. solution of β -naphthalenesulphonic acid. The mixture is warmed to 70—80°, then made up to 100 c.c. with water, and filtered through a dry paper. Fifty c.c. of the liquid are boiled for 6 minutes with 50 c.c. of Fehling's solution, and after the cuprous oxide has settled, the supernatant liquid is poured off. The cuprous oxide is transferred to a tube by means of as little water as possible and to it is added 10 c.c. of an alkaline solution of Rochelle salt and 0.5 gram of hydrazine sulphate. The tube is placed in a thermostat, and when the temperature equilibrium has been established it is connected with a nitrometer. The contents of the tube are boiled for two minutes and the tube replaced in the thermostat. Nitrogen is evolved according to

the equation: $\text{N}_2\text{H}_4 + 2\text{Cu}_2\text{O} = 2\text{H}_2\text{O} + \text{N}_2 + 4\text{Cu}$. From the volume of nitrogen the weight is found, and from a table given the weight of lactose in 5 c.c. of the milk is obtained:

| | | |
|-----------------|---|-------------------|
| 10 mg. nitrogen | = | 64.8 mg. lactose. |
| 15 " | | 98.4 " |
| 20 " | | 132.7 " |
| 25 " | | 167.0 " |
| 30 " | | 202.0 " |
| 35 " | | 237.9 " |
| 40 " | | 274.3 " |

J. McC.

Analysis of Explosives. By F. W. SMITH (*J. Amer. Chem. Soc.*, 1901, 23, 585—589).—*Estimation of sulphur in gelatin dynamite.*—Two grams of the sample are introduced into a 100 c.c. silver crucible filled two-thirds with an alcoholic solution of sodium hydroxide. The mixture is heated until the nitroglycerol is decomposed and then evaporated to dryness. Forty grams of potassium hydroxide and 5 grams of potassium nitrate are added and the whole is fused until all organic matter is burnt. The mass is then dissolved in dilute acetic acid and the sulphuric acid estimated as usual.

Indirect estimation of nitroglycerol in gelatin dynamite, &c.—Fifteen grams of the sample are extracted with chloroform in a Soxhlet apparatus and the loss in weight is noted; in another portion, the moisture is determined by desiccation over sulphuric acid for 5 days. Another portion of 2 grams is carefully extracted by maceration with ether in a small beaker. The ether is poured through a filter, the extraction repeated three or four times, the ethereal solution allowed to evaporate and the residue mixed with 5 c.c. of ammonium sulphide and 10 c.c. of alcohol. After heating gently on the water-bath until the nitroglycerol is decomposed, 250 c.c. of water and a slight excess of hydrochloric acid are added and the precipitate is first washed free from acid and then extracted with alcohol and chloroform, the filtrate being collected in a weighed platinum dish. After evaporating and drying at 50°, the contents are weighed and then transferred to a silver crucible and examined for sulphur in the manner first described. The weight of the residue less the sulphur represents the substances soluble in chloroform in the original sample except nitroglycerol, moisture, and sulphur. The percentages of the former substances *plus* the moisture and sulphur in the original sample deducted from the total matter soluble in chloroform are equal to the percentage of nitroglycerol. In another portion, the residue in the platinum dish may be examined for resins, paraffin, &c.

Use of Lunge's nitrometer.—This is best standardised by the "empirical method." Nitric oxide, derived from a known amount of pure potassium nitrate, is passed into the measuring tube and the quantity of air in the reduction tube is then varied until the volume of the nitric oxide is approximately the calculated amount. The reduction tube is now sealed, a series of tests made with slightly varying amounts of potassium nitrate, and in each case a correction factor determined which shows 100 per cent. in purity in the

nitrate taken. A sample of pure dry nitroglycerol may also be used. The extreme variations in the determinations should not exceed 0.05 per cent. From the average of the determinations, a correction factor is obtained, which is then applied to all determinations. The sulphuric acid best suited for nitrometer work contains 94—95 per cent. of acid.

L. DE K.

Estimation of Glycogen. By ALFONS BUJARD (*Zeit. Nahr.-Genussm.*, 1901, 4, 781).—Lebbin's process (this vol., ii, 45) is not based on a new principle, as the author since 1897 has made use of alcoholic potash to separate proteids from glycogen in the following way. The meat is dissolved in 8 per cent. alcoholic potash, diluted with 50 per cent. alcohol and the insoluble residue well washed with the latter. The crude glycogen is then dissolved in 8 per cent. aqueous potash, filtered, faintly acidified with acetic acid, and precipitated with alcohol. The precipitate requires no further purification. L. DE K.

Occurrence and Estimation of Lactic Acid in Wines. By RUDOLF KUNZ (*Zeit. Nahr.-Genussm.*, 1901, 4, 673—683).—Two hundred c.c. of wine are mixed with a slight excess of powdered barium hydroxide and evaporated to about two-thirds of the original volume. When cold, the whole is rinsed into a 200 c.c. flask, which is then filled up to the mark; 150 c.c. of the filtrate are evaporated to a thin syrup after neutralising the excess of baryta with carbon dioxide, and when cold, excess of dilute sulphuric acid is added, and the whole introduced into a Schacherl extraction apparatus where the liquid is extracted with ether for 18 hours. The ether in the extraction flask is now driven off by warming after 30 c.c. of water have first been introduced. The aqueous solution is then distilled in a current of steam until all the volatile acids have passed over and the residue, after adding a few drops of phenolphthalein, is mixed with a slight excess of barium hydroxide. If after 15 minutes' warming on the water-bath the alkaline reaction is still persistent, a current of carbon dioxide is passed and the filtrate concentrated to 10 c.c. After introducing this into a 150 c.c. flask and using 40 c.c. of water for rinsing, the liquid is made up to the mark by adding 95 per cent. alcohol. One hundred c.c. of the filtrate are evaporated on the water-bath, and the residue is rinsed into a beaker, acidified with hydrochloric acid, and precipitated with sodium sulphate. From the weight of the barium sulphate, the corresponding amount of lactic acid contained in 100 c.c. of wine is readily calculated. Experiments are communicated in support of the method and to prove that the lactic acid extracted from wines is really the pure substance.

A table is given containing the amount of total acidity calculated as tartaric acid, potassium hydrogen tartrate, tartaric acid, volatile acids calculated as acetic acid, succinic acid, lactic acid, amount of c.c. of $N/2$ alkali used for neutralising 100 c.c. of wine, amount of alkali corresponding with the acids determined and alkali consumed by undetermined acids. Twenty-three samples were tested in this way, the lactic acid varying from 0.1185 to 0.4360 gram in 100 c.c.

L. DE K.

Estimation of β -Hydroxybutyric Acid in Urine. By PETER BERGELL (*Zeit. physiol. Chem.*, 1901, 33, 310—311).—The estimation of β -hydroxybutyric acid in urine may be accomplished much more readily if in the Magnus-Levy method (*Arch. exp. Path. Pharm.*, 45, 390) the dried residue from the urine is extracted with ether in a Soxhlet apparatus instead of the urine itself being extracted by shaking with ether. To obtain the dried residue, 100—300 c.c. of urine are rendered slightly alkaline with sodium carbonate and evaporated to a syrup; this is cooled, and mixed with syrupy phosphoric acid, then with 20—30 grams of finely divided and ignited copper sulphate and 20—25 grams of fine sand. J. J. S.

Detection of Citric Acid in Wine. By MATTEO SPICA (*Gazzetta*, 1901, 31, ii, 61—67).—One hundred c.c. of the wine are evaporated on the water-bath to a syrup which is extracted repeatedly with small quantities of alcohol, the liquid being filtered through a dry filter and alcoholic potassium hydroxide added in such quantity as to leave the solution faintly acid. After a few minutes, the liquid is filtered to remove the separated potassium tartrate, and then exactly neutralised with alcoholic potassium hydroxide. If citric acid is present, a white precipitate, consisting of potassium citrate and potassium hydrogen tartrate, is formed and is filtered, dried, and heated gently in a dry test-tube with a very small quantity of sulphuric acid until bubbles of gas are evolved. After cooling and diluting with water, the liquid is rendered alkaline with potassium hydroxide, the mixture being kept cold. If citric acid was present in the wine taken, the liquid now obtained contains small quantities of acetone, and on adding sodium nitroprusside, a blood-red coloration is formed, which changes to reddish-violet on adding acetic acid. In case the wine contains no citric acid, the addition of the sodium nitroprusside causes the formation of a yellowish-green coloration, due to the presence of tartaric acid. T. H. P.

Detection and Estimation of small quantities of Salicylic Acid in Wines and Foods. By HENRI PELLET (*Ann. Chim. anal. appl.*, 1901, 6, 327—328).—Two hundred c.c. of the wine are rendered alkaline and concentrated to, say, one-tenth, and the liquid is then treated by the method proposed by the author and Grobert. In this manner, 0.01 gram of salicylic acid in 100 litres of wine may be detected and estimated.

The extraction with ether is always attended with loss, the amount of which must be ascertained by testing pure samples to which a known quantity of salicylic acid has been purposely added (see following abstract). L. DE K.

Nature of the Substance giving the Ferric Chloride Reaction; Presence of Salicylic Acid in Pure Wines. By HENRI PELLET (*Ann. Chim. anal. appl.*, 1901, 6, 328—331).—Ferreira Da Silva (this vol., ii, 291) has stated that Pellet and Grobert's method for the detection of salicylic acid is not trustworthy, as it may sometimes show traces of this substance when it is absent. It now appears, however, that there is every reason to believe that the substance which gives

the reaction is really salicylic acid, or in other words, that salicylic acid is a natural constituent of some kinds of Portuguese wine. It will now be necessary to investigate this matter fully, and to arrive at a limit beyond which a sample may be pronounced adulterated.

L. DE K.

Oil of Citron. By HERBERT E. BURGESS (*Analyst*, 1901, 26, 260—262).—The author has been able to procure an undoubtedly genuine specimen of oil of citron or "essence de cedrat." The commercial article is generally oil of lemon, "essence de citron," with some verbenä. The analysis differs considerably from those obtained by other workers, as will be seen by referring to the table in the original paper.

The oil has a sp. gr. 0.8513 at 15°; n_D 1.4750 at 20°; $[\alpha]_D$ (100 mm.) +80°13'. On distilling the oil at a pressure of 10 mm., three fractions were obtained. No. 1, b. p. 60—62°, constituting 12 per cent. of the sample, had a rotation of +86°30'; No. 2, b. p. 62—64°, amounting to 80 per cent., a rotation of +85°30'; and No. 3, b. p. 64—85°, amounting to 5 per cent., a rotation of +13°30'. Nos. 1 and 2 were refractionated over sodium, and the main fraction was identified as limonene, b. p. 173—174° under atmospheric pressure. No. 3 was proved to consist of citral. This was also determined in the original sample by the sodium hydrogen sulphite and the hydroxylamine methods, which showed respectively 6.2—5.8 and 5.7 per cent. of citral.

A crystalline deposit purified by chloroform, light petroleum, and recrystallisation from alcohol gave on analysis figures corresponding with those required for the formula $C_{18}H_{18}O_6$; this substance is probably the same as that observed by Crismer and more recently by Theulier.

L. DE K.

Estimation of the Acidity in Fodder Fats. By GUSTAV LOGES and KURT MÜHLE (*Landw. Versuchs-Stat.*, 1901, 56, 95—96. Compare Emmerling, *ibid.*, 49, 45; Abstr., 1891, 770, and 1893, ii, 38).—The finely-ground substance (5 grams) was agitated with 100 c.c. of water and ether for 30 minutes in a Wagner rotatory apparatus and a portion of the filtrate titrated with alcoholic potash (made with 50 per cent. alcohol). On comparing the results with those obtained by titrating dried ether extracts of the same foods (cakes and meals), it was found, as previously, that the latter method gave much lower results. This is more especially the case with old samples, and it may, perhaps, be possible to discriminate between fresh and stored foods by determining the acidity by the two methods.

N. H. J. M.

Detection of Coconut Oil in Butter. By FERNAND RANWEZ (*Rev. Intern. Falsific.*, 1901, 14, 89—94).—A critical examination of some processes recommended of late for the detection of coconut oil in butter. Of these the only one likely to be of service is the process proposed by Vandam (*Ann. Pharm.*, 1901, 201), based on the fact that coconut oil contains a large proportion of volatile acids which are insoluble in water but soluble in rectified spirit. The process should be thoroughly investigated.

L. DE K.

Detection of Sesamé Oil in Chocolate. By GIOVANNI POSSETTO (*Chem. Centr.*, 1901, ii, 236; from *Giorn. Farm. Chim.*, 51, 241—245).—Sesamé oil is best detected by Baudouin's sugar test. To apply this to chocolate, 20—25 grams of the sample are boiled for 5 minutes with 50 c.c. of ether, and after a short time has elapsed the filtrate is evaporated to dryness and the residual fat heated for some hours to 95° in order to separate the colouring matter. The fat is then filtered whilst hot, and 5—6 grams of the clear liquid are shaken with an equal volume of a solution of sugar in hydrochloric acid. In the presence of sesamé oil, the characteristic magenta coloration makes its appearance.
L. DE K.

Estimation of Formaldehyde. By A. G. CRAIG (*J. Amer. Chem. Soc.*, 1901, 23, 638—643).—Several methods are criticised, Legler's process being finally preferred. This process, with a slight modification introduced by the author, is as follows. A quantity of the sample representing about 0.5 gram of pure formaldehyde is placed in a 3 oz. pressure bottle fitted with a soft rubber stopper, and 25 c.c. of approximately normal ammonia are added; in a similar bottle, 25 c.c. of normal ammonia only are introduced. Both are then placed up to the neck in a bath of boiling water for one hour and when cold they are carefully titrated with normal sulphuric acid, using methyl-orange as indicator. The difference between the determinations represents the formaldehyde, being 0.0601 gram for each c.c.
L. DE K.

Estimation of Formaldehyde. By ZDENĚK PEŠKA (*Chem. Zeit.*, 1901, 25, 743).—Legler's ammonia process gives good results if the excess of ammonia is carefully titrated, using litmus as indicator, the end reaction being observed by noticing the disappearance of the blue colour without getting the so-called neutral colour.

Romijn's iodometric process (*Abstr.*, 1987, ii, 166), oxidation of formaldehyde to formic acid in alkaline solution, is said to be the most satisfactory method and preferable to the one proposed by Blank and Finkenbeiner (see following abstract).
L. DE K.

Estimation of Formaldehyde. By OSKAR BLANK and HERMANN FINKENBEINER (*Chem. Zeit.*, 1901, 25, 794).—The authors call attention to their method of estimating formaldehyde by means of hydrogen peroxide (*Abstr.*, 1899, ii, 188, 820). The results agree well with those obtained by the iodometric method, and the process is easy of execution. Legler's ammonia method and the sodium hydroxide process are untrustworthy.
L. DE K.

Modification of the Sulphuric Acid Test for Formaldehyde in Milk. By A. GUSTAV LUEBERT (*J. Amer. Chem. Soc.*, 1901, 23, 682—683).—Five grams of the suspected sample of milk are distributed over 5 grams of coarsely powdered potassium sulphate contained in a 100 c.c. flask and 10 c.c. of sulphuric acid are then poured down the side of the flask. If formaldehyde is present, the potassium sulphate becomes violet in a few minutes, the colour gradually dispersing through the entire liquid, but if it is absent the liquid assumes at once a brown colour, rapidly changing to black.

By this process, 1 part of formaldehyde may be detected in 250,000 parts of milk. L. DE K.

Detection of "Saccharin." By F. WIRTHLE (*Chem. Zeit.*, 1901, 25, 816. Compare this vol., ii, 135).—If the colour produced with ferric chloride should be a dirty brown, the liquid is acidified and again shaken with ether-petroleum mixture; this is then shaken three times with 20 c.c. of water and evaporated to dryness, when the test with ferric chloride is again applied. If there still exists a doubt, another experiment should be made as follows: 200 c.c. of wine are mixed with 40—50 drops of a 10 per cent. solution of ferric chloride and then digested on the water-bath with a slight excess of freshly precipitated calcium carbonate. The filtrate, which is now free from tannins, is tested as described; 0.5 milligram of "saccharin" may thus be detected. L. DE K.

Detection of "Saccharin" by means of New Reactions. By MATTEO SPICA (*Gazzetta*, 1901, 31, ii, 41—46).—The author has devised two methods for the detection of small proportions of 'saccharin' in commercial products. The first of these consists in converting the imino-group of the 'saccharin' into nitric acid, which is recognised by means of diphenylamine hydrochloride, whilst in the second method the 'saccharin' is transformed into one of the sulphaminobenzoic acids which can be detected by the diazo-reaction. The method of working is as follows. The liquid to be tested, acidified with sulphuric acid, or in the case of a solid, the extract obtained with the dilute acid, is shaken in a separating funnel with ether or a mixture of ether and light petroleum, the liquid being then filtered and divided amongst three dry test-tubes which are placed in a water-bath to evaporate. The residue in one tube is tested for salicylic acid by adding nitric acid and heating gently to form picric acid, which is recognised by the method previously described (*Abstr.*, 1895, ii, 426). To the second residue is added a little lime, best somewhat granular as obtained from powdered marble, and the mixture then heated until it becomes slightly brown; a few c.c. of water are then added, the liquid heated to boiling, and the clear solution decanted off into another tube, where it is mixed with a few drops of hydrochloric acid and a small piece of zinc; after hydrogen has been evolved for 20 minutes, the liquid is again decanted off and to it are added a few drops of dilute sodium or potassium nitrite solution and 5 to 6 drops of α -naphthylamine hydrochloride solution; in the event of 'saccharin' being present in the substance examined, a crimson coloration is obtained which only appears after some hours if the quantity of 'saccharin' is very small. To the residue in the third tube are added a few drops of pure sulphuric acid and a crystal of potassium permanganate, oxidation being started by gentle heating, and the excess of permanganate removed by means of oxalic acid or sulphur dioxide. The liquid is then diluted with a few c.c. of water, a few drops of diphenylamine hydrochloride are added, and pure sulphuric acid poured carefully down the side of the test-tube so as to form a distinct layer at the bottom. The presence of nitric acid,

produced from 'saccharin,' is manifested by an azure-blue ring in the layer between the sulphuric acid and the aqueous liquid. T. H. P.

Estimation of Urea in Urine. By JOHN H. LONG (*J. Amer. Chem. Soc.*, 1901, 23, 632—638).—In order to obtain exact results with Liebig's mercuric nitrate process, allowance should be made, not only for the presence of sodium chloride, but also for the ammonia, uric acid, and creatinine. By careful analyses, the author has found that the average error due to ammonia is 1 c.c. of the mercury solution when titrating 10 c.c. of urine; uric acid is responsible for 0.15, and creatinine for 0.85 c.c.; total, 2 c.c. of mercury solution to be deducted. These figures apply only to fresh urine. L. DE K.

General Reaction of the Aromatic Amines and Hydrazines with Wood. By ERCOLE COVELLI (*Chem. Zeit.*, 1901, 25, 684).—*Amines.*—It is known that aniline gives a yellow coloration with fir wood. The author states that all aromatic amines give a reaction. The test is best applied by dissolving traces of the amines in hydrochloric acid, and moistening a shaving of fir wood. Aniline, methylaniline, *o*-toluidine, and *p*-toluidine cause a yellow colour resembling that of arsenic trisulphide. Sulphanilic acid, *o*-, *m*-, and *p* chloroaniline, *o*- and *p*-aminophenol, phenetidine, orthoform, aminosalicylic acid, diphenylamine, *m*-phenylenediamine, α -naphthylamine, and *o*- and *p*-aminobenzoic acids cause an orange-yellow colour; *o*- and *m*-nitroaniline, diamino-phenol, triaminophenol, *p*-nitroaniline, and *p*-phenylenediamine give an orange-red colour. When acid-groups are introduced (acetanilide, lactophenine, &c.), the wood is no longer coloured. Ammonia removes the colour.

Hydrazines.—A solution of phenylhydrazine in hydrochloric acid gives with fir wood a yellow colour which turns red and finally green after a few hours; on adding ammonia, it changes again to red, but becomes green on adding acid. This is a very characteristic reaction for phenylhydrazine.

p-Tolylhydrazine and α -naphthylhydrazine first give a yellow and then a red colour which turns brownish after some hours.

The active substance contained in the wood is oxidised by chlorine water; if a piece of paper containing wood-pulp is immersed for 24 hours in chlorine water, it loses its property of reacting with amino-compounds. Pyrrole, indole, and carbazole give with wood a reddish colour which disappears on moistening with ammonia. L. DE K.

Formation of Carbamide by the Oxidation of Physiological Nitrogenous Substances by means of Permanganate in Acid Solution. By W. FALTA (*Ber.*, 1901, 34, 2674—2679).—The method adopted by Jolles (*Abstr.*, 1900, ii, 636) for the oxidation of nitrogenous substances, according to which the acid solution is boiled for 10 hours and then evaporated, itself leads to the decomposition of the greater part of any carbamide present or produced in the liquid. Hippuric acid and asparagine do not yield carbamide when oxidised by permanganate in acid solution, and the substance obtained by Jolles as a product of their oxidation, and believed by him to be carbamide

oxalate, is, in reality, a mixture containing ammonium salts and compounds of manganese. Uric acid yields a certain proportion of carbamide, along with a considerable proportion of ammonia. A. H.

Behaviour of Acid Aqueous Solutions of Alkaloids [Glucosides, &c.] towards different Solvents. By HANS PROELSS (*Chem. Centr.*, 1901, 11, 236—237; from *Apoth. Zeit.*, 16, 434—435).—The following solvents were tried: ether, chloroform, ethyl acetate, benzene, and mixtures of ether or alcohol with chloroform. Of alkaloids, &c., the following were tested, 5 c.c. of an aqueous solution (1 in 500) being used. Digitalin, colchicine, picrotoxin, brucine, veratrine, strychnine, atropine, codeine, and morphine. To render the liquid acid, a few drops of dilute hydrochloric acid were added, and alkalinity was imparted by means of sodium carbonate or ammonia. It was shown that chloroform is the best general solvent. Sodium carbonate and ammonia may be used for brucine, strychnine, atropine, and codeine; ammonia should be used for veratrine and morphine. Colchicine is readily extracted from an acid solution by chloroform; digitalin from an acid solution by chloroform or chloroform-ether mixture; picrotoxin from an acid solution by ether-chloroform, alcohol-chloroform, or benzene; brucine from an alkaline solution by ether-chloroform; veratrine from a solution mixed with sodium carbonate by ether-chloroform, alcohol-chloroform, chloroform, or ethyl acetate, and from an ammoniacal solution by ether or benzene; strychnine from an alkaline solution by chloroform, alcohol-chloroform, or benzene; atropine from an alkaline solution by chloroform, alcohol-chloroform, ether-chloroform, or benzene; codeine from an alkaline solution by alcohol-chloroform, benzene, or ethyl acetate; morphine from an ammoniacal solution by ethyl acetate, and from a solution containing potassium hydrogen carbonate by alcohol-chloroform. Emulsions are mostly formed when benzene is used, and more rarely when ether or ethyl acetate is employed. L. DE K.

Resisting Power of Alkaloids, Glucosides, and Bitters to Putrefaction. By HANS PROELSS (*Chem. Centr.*, 1901, ii, 503; from *Apoth. Zeit.*, 16, 492—493).—Five hundred grams of meat and blood were mixed with 0.5 gram of mixed brucine and strychnine; mixtures were also made containing 0.5 gram of mixed morphine and strychnine, codeine, atropine, veratrine, colchicine, digitalin, picrotoxin, and finally, one with 2 grams of opium. After being exposed to the air in glass vessels for 14 days, these were put in a box which was securely nailed down and buried 20 c.m. deep in the earth. After four months and a half, the box was unearthed, the contents of each glass vessel were well mixed, and 100 grams of the material were used in the testing. The following poisons were sharply detected: strychnine, brucine, codeine, colchicine, veratrine; feebly: picrotoxin, digitalin, opium alkaloids, morphine; atropine could not be detected. After being again buried for three months and a half, another 200 grams were tested, and colchicine, brucine, veratrine, strychnine, codeine, and morphine could still be detected. Strychnine and brucine may be tested for in each other's presence, but not strychnine and morphine. That the morphine was so stable may be explained by the fact that

it had been simply mixed with the putrefying mass, whilst in previous experiments it had been introduced into the living organism; this circumstance also affects the limit of time within which other alkaloids may be recognised.

L. DE K.

Estimation of Aconitine in Preparations of Aconite. By H. ECALLE (*J. Pharm. Chim.*, 1901, [vi], 14, 97—102).—Bertrand (Abstr., 1899, ii, 456) has stated that when silicotungstic acid is added to a solution of aconitine, a precipitate is obtained of the composition $12\text{WO}_3, \text{SiO}_2, 2\text{H}_2\text{O}, 4\text{A}, n\text{H}_2\text{O}$, where A is the alkaloid. The author finds that this precipitate is better represented by the formula $12\text{WO}_3, \text{SiO}_2, 2\text{H}_2\text{O}, 3\frac{1}{2}\text{A}, n\text{H}_2\text{O}$. In order to estimate the aconitine in extract of aconite, excess of ammonia is added to a solution of the extract in dilute nitric acid, and the alkaloid removed by shaking repeatedly with ether. The ethereal solution is shaken with dilute nitric acid, the acid solution warmed to expel dissolved ether, and, when cold, treated with a solution of silicotungstic acid. The mixture is heated until it boils, and left for 24 hours; the precipitate is then collected, washed, dried, and ignited. The weight of the alkaloid is obtained by multiplying the weight of the residue, $12\text{WO}_3, \text{SiO}_2$, by 0.793. Estimations of the alkaloid in different commercial specimens of tincture and extract of aconite show that the amount is liable to great variation.

E. G.

Microchemical Reaction for Atropine. By N. SCHOORL (*Chem. Centr.*, 1901, ii, 560; from *Nederl. Tijdschr. Pharm.*, 13, 208—209).—Tropine, the product of hydrolysis of atropine, yields a very characteristic hydriodide. The alkaloid is heated with a drop of aqueous sodium hydroxide, and the vapours are condensed on an object glass. A little hydrochloric acid is added, the liquid is evaporated, the residue dissolved in a drop of water, and a small particle of potassium iodide added. The tropine hydriodide thus obtained forms well defined needles and plates.

L. DE K.

Extraction of Morphine with Immiscible Solvents. By WILLIAM A. PUCKNER (*J. Amer. Chem. Soc.*, 1901, 23, 470—473).—A large number of experiments are communicated showing that morphine may be removed from a very slightly ammoniacal solution by repeated agitation with an equal volume of a mixture of 80 volumes of chloroform and 20 volumes of alcohol. If a somewhat large excess of ammonia is present, this may be neutralised by addition of sodium hydrogen carbonate. Addition of ammonium chloride is unnecessary. A solution of morphine in the slightest possible excess of sodium hydroxide yields only a little alkaloid to the alcohol-chloroform mixture, and in the presence of more alkali scarcely any of the alkaloid is extracted; on adding sodium hydrogen carbonate, the morphine is, however, liberated and rendered soluble (compare Wirthle, this vol., ii, 362).

L. DE K.

Estimation of Morphine in Opium by means of Ammoniacal Silver Chloride. By C. REICHARD (*Chem. Zeit.*, 1901, 25, 816—818).—The process is based on the fact that of the numerous

soluble constituents of opium, morphine is the only substance capable of quantitatively reducing an ammoniacal solution of silver chloride; 2 atoms of metallic silver represent 1 mol. of crystallised morphine.

A definite weight of opium powder is treated with 10—20 times its weight of boiling water and the mixture is frequently stirred for an hour. The liquid is filtered and the insoluble matter washed with hot water. To the united filtrates is now added a solution of silver chloride in ammonia and the whole is at first gently heated, although this is not strictly necessary. After a few hours, the precipitation is complete and the reduced silver is then collected on a filter and washed until the filtrate is no longer affected by ammonium sulphide. The filter is dried at 130°, burnt in a porcelain crucible, and the metallic silver weighed.

It is advisable to make another aqueous infusion and to precipitate the morphine by a judicious quantity of ammonia; the filtrate should have no reducing properties.

L. DE K.

Estimation of Nicotine in Tobacco. By JULIUS TÓTH (*Chem. Zeit.*, 1901, 25, 610. Compare this vol., ii, 203).—Experiments are communicated showing that practically no ammonia passes into the ether-petroleum mixture. Keller's proposal to remove such traces by blowing air through the liquid for one minute cannot be recommended, as this causes a slight loss of nicotine.

L. DE K.

Analysis of Tanning Materials. By GIUSEPPE SESTI (*Chem. Centr.*, 1901, ii, 745—746; from *Staz. sperim. agrar. ital.*, 1901, 34, 346—358).—Solutions containing tannin should not be filtered through paper but through asbestos, or filtration may be avoided by allowing a sufficient time for the liquid to settle. The following process is applied to the analysis of sumach. Five grams of the powder are extracted with hot water and when cold diluted to 500 c.c., or they are mixed with 500 c.c. of water and digested for 48 hours. Ten c.c. of the clear solution are then withdrawn and diluted to 400 c.c.; 10 c.c. of dilute sulphuric acid and 20 c.c. of solution of indigo-carmin are added, and the liquid titrated with $N/20$ potassium permanganate. In the meanwhile, 20 c.c. of the filtered solution are mixed with 10 c.c. of ammoniacal copper solution (22 grams of copper sulphate dissolved in 1 litre of ammonia; 1 c.c. precipitates 0.014 gram of tannin) and diluted to 200 c.c. One hundred c.c. of the filtrate are then diluted to 400 c.c. and titrated as before; the difference in c.c. of permanganate between the two titrations multiplied by 2.078 represents the percentage of tannin in the sumach.

L. DE K.

Commercial Valuation of Tanning Materials and a New Method for the Detection and Estimation of Gallic Acid in them. By MATTEO SPICA (*Gazzetta*, 1901, 31, ii, 201—208).—The author discusses the various methods proposed for the detection and estimation of gallic acid and gives the following new ones.

For detecting the acid, the material is extracted with boiling water and the solution treated in a test-tube with a slight excess of potassium plumbite; the liquid is shaken repeatedly, poured into a beaker and diluted with distilled water, which produces a more or less

intense crimson-red coloration according to the amount of gallic acid present.

To determine the proportion of gallic acid present, a weighed quantity of the material is treated with boiling water in amount sufficient to give a solution of 1—2 parts of gallic acid per 1000, and the volume of the solution measured. To 10 c.c. of the liquid are added about 5—10 c.c. of a potassium plumbite solution of sp. gr. 1.20, the solution being then either repeatedly shaken to aerate it or mixed with a few centigrams of potassium persulphate and finally made up to 100 c.c. At the same time, 10 c.c. of a solution of 1 part of gallic acid in 1000 are treated in the same way. Ten c.c. of each of the two solutions are poured into the cells of a Salleron colorimeter and compared. If the coloration is the same in the two cases, equal quantities of gallic acid are present in the two solutions. If this is not the case, water is added from a burette to the liquid which is the more intensely coloured until it has the same density of colour as the other. On reading off the amount of water added, the calculation of the percentage of gallic acid in the material taken can be readily carried out. The numbers obtained by this method are lower than those yielded by the permanganate method usually employed. T. H. P.

Estimation of Humus in Soil. By KURT BIELER and K. ASÖ (*Bull. Coll. Agr. Tokyo Imp. Univ.*, 1901, 4, 237—240).—Humus was determined by four different methods, (1) by combustion and multiplying the carbon result by 0.471, (2) by Knop's method, (3) by extracting successively with dilute hydrogen chloride and 3 per cent. ammonia and deducting the weight of ash from that of the ammonia residue, and (4) by Aschmann and Faber's volumetric method (*Abstr.*, 1900, ii, 60). The following amounts of humus were found by the different methods: (1) 13.84, (2) 8.85, (3) 9.79, and (4) 6.95 per cent. N. H. J. M.

The Bromination and Iodination Numbers of Proteids. By WILHELM VAUBEL (*Zeit. anal. Chem.*, 1901, 40, 470—474).—It has been shown by Blum and Vaubel (*Abstr.*, 1898, i, 287, 609) that when albumin, casein, &c., are treated with halogens, a larger quantity of the haloid acid is obtained than corresponds with the halogen which replaces hydrogen in the proteid. They therefore distinguish between the bromine (or iodine) number, and the bromination (or iodination) number, the latter being the total amount of halogen consumed, and being more easily ascertained than the former. In neither case does a single treatment complete the substitution, but for comparable results a single treatment is sufficient. With bromine, the action proceeds much further than with iodine. The process employed consisted in dissolving 2 grams of the proteid in 200 c.c. of water, adding sodium bromide, 200 c.c. of glacial acetic acid, and 20 c.c. of hydrochloric acid, and then bromate solution until an excess, persisting for 15 minutes, was shown by iodide-starch paper. Allowing 9 per cent. for the bromine consumed in substitution, the three proteids showed a further consumption, namely, egg-albumin, 35.04; blood albumin, 40.76; and casein, 27.00 parts of bromine per cent. M. J. S.

Detection of Minute Traces of Albumin in Urine. By A. PRAUM (*Chem. Centr.*, 1901, ii, 322; from *Deutsch. med. Zeit.*, 27, 220).—A few c.c. of the filtered urine are mixed with a few drops of a concentrated solution of sulphosalicylic acid, and a little more of the filtered urine is carefully poured down the sides of the test-tube. Operating in this manner, any difference in the turbidity of the two layers will be readily noticed.
L. DE K.

Sulphosalicylic Acid as a Test for Albumin. By G. ROCH (*Chem. Centr.*, 1901, ii, 445; from *Pharm. Centr.-Halle*, 42, 393).—This reagent, recently recommended by Praum (preceding abstract), has been used for a long time by the author (*Pharm. Centr.-Halle*, 30, 549). It is best prepared by warming 13 grams of salicylic acid with 20 grams of sulphuric acid and dissolving the product in 67 grams of water; the slight excess of sulphuric acid does not affect the result. By means of this test, as little as 0.0025 per cent. of albumin may be detected in urine.
L. DE K.

Detection of Peptone in Urine and Fæces. By O. FREUND (*Chem. Centr.*, 1901, ii, 505; from *Centr. inn. Med.*, 22, 647—651).—When testing for peptones in urine, it is necessary to completely remove urobilin. According to the author, this may be satisfactorily effected by adding to 10 c.c. of urine 2 or 3 drops of 20 per cent. acetic acid, 5 c.c. of 20 per cent. solution of lead acetate or basic lead acetate, boiling, and filtering. To the filtrate is then added aqueous potassium hydroxide so long as this produces a precipitate, and the liquid is again boiled and filtered. The filtrate may now be used for the biuret test. The same process applies to liquid fæces. The presence of urobilinogen does not interfere; this may, moreover, be converted into urobilin by means of iodine or nitrous acid, and then removed by lead as directed.
L. DE K.

Pancreatic Rennin and Diastase. By HORACE M. VERNON (*J. Physiol.*, 1901, 27, 174—199).—The rennin ferment in pancreatic extracts is estimated by determining the time of onset of Roberts' 'metacasein reaction,' and the diastatic by the time required for starch solution to reach the 'achromic point' when tested with iodine. The metacasein reaction depends on the rennin, not on the trypsin in the extract; it bears no relation to the tryptic power of the extract, but there is a fairly constant relationship between it and the milk curdling capacity of the extracts.

The time of onset of the two reactions mentioned varies inversely as the one-sixth power of the amount of ferment present. This proportion is, however, upset by the addition of 0.1 per cent. of sodium chloride, or by the use of tap water instead of distilled water in making the solutions of starch. The diastatic activity is increased by small quantities of acid, but is inhibited by 0.009 per cent. of hydrochloric, 0.04 per cent. of lactic, and 0.16 per cent. of acetic acid.

Extracts kept for several hours at 38° undergo loss of power on milk. The rate of destruction varies with the activity of the original solution. Hence it is concluded that rennin, like trypsin, is not a single chemical substance. The diastatic ferment is destroyed at the same rate whatever its initial activity.
W. D. H.

Absorption Spectra of the Colouring Matters of Blood. By JULIUS FORMÁNEK (*Zeit. anal. Chem.*, 1901, 40, 505—523).—The position of the bands in the absorption spectra of the blood colouring matters is indicated in the present paper by the wave-length corresponding with the maximum darkness, which is not dependent (as the positions of the edges of the bands are) on the concentration of the solution or the thickness of the layer.

Blood, simply freed from fibrin and suitably diluted, gives the two bands of oxyhæmoglobin at λ 578.1 and λ 541.7. After standing for some days exposed to air and light, a new band at λ 634, due to methæmoglobin, becomes visible: the amount of the latter substance increases with time and a feeble band at λ 500.8 is developed. If yellow ammonium sulphide or Stoke's reagent is added to the diluted blood, hæmoglobin is produced, which gives one broad band at λ 554.7 and sometimes a feeble one at λ 619.8 due to sulphohæmoglobin. When a dilute acid is added to blood the oxyhæmoglobin splits into albumin and acid hæmatin. The latter gives three bands, at λ 554.8, 517.7, and 654.2, the last visible only with strong solutions. Alkaline hæmatin, obtained by the action of concentrated potash in the cold, gives two indistinct bands at λ 582 and 546.5; after heating nearly to boiling and adding water, only a single feeble band at 580.7 can be observed, but if alcohol is added instead of water a more intense absorption, varying in position between 597.4 and 600.2 results. If the diluted blood, mixed with potassium hydroxide, is heated to 70° whilst observing with the spectroscope, an intense band at 559.1 and a feeble one at 529.2 come into view as those at 582 and 546.5 disappear: this is the spectrum of reduced hæmatin resulting from the action of a trace of potassium sulphide, produced by the decomposition of the albumin by the alkali. The same spectrum of reduced hæmatin is obtained if the alkaline blood is left for an hour or two in the cold, or when ammonium sulphide is added to either acid or alkaline hæmatin.

On adding concentrated sulphuric acid to blood and warming, hæmatoporphyrin is produced, which in acid solution gives two bands whose position varies between 553—558 and 599—604.5 respectively: the addition of a small excess of alkali produces a spectrum of four intense bands, also somewhat variable in position. If hydrogen sulphide and air are simultaneously passed through diluted blood, sulphohæmoglobin results; this gives a sharp band at 619.8. All the above colouring matters absorb the blue and violet of the spectrum to a greater or less extent.

Of the above spectra, those of reduced hæmatin and of acid hæmatoporphyrin, especially the former, are the most sensitive for the recognition of old or minute blood stains. Very old stains, in which the hæmoglobin has become insoluble, can be dissolved by potassium cyanide solution, and on adding excess of ammonium sulphide to this solution reduced hæmatin is obtained.

Observations of the spectrum of blood containing carbon monoxide show that the spectra are all compromises, the bands of carbonyl hæmoglobin, which lie nearer to the blue end than those of oxyhæmoglobin, blending with those of the latter substance to give intermediate

bands, the position of which depends on the amount of carbon monoxide absorbed.

Charts of the above spectra and a large amount of detailed information on the whole subject are given in the paper. M. J. S.

New Instrument for the Estimation of the amount of Hæmoglobin in Blood. By GUSTAV GAERTNER (*Monatsh.*, 1901, 22, 745—747).—The method depends on the fact that hæmoglobin absorbs the chemically active rays of the spectrum. The effect of light transmitted through a given thickness of blood, on a photographic plate, is inversely proportional to the amount of hæmoglobin present. The paper must be consulted for details of the apparatus.

K. J. P. O.

Hæmoglobin Crystals for the Distinction between Human and Animal Blood. By MOSER (*Chem. Centr.*, 1901, ii, 858—859; from *Vierteljahres-schr. ger. Med. öffentl. Sanitätswes.*).—The author has experimented with human blood and the blood of various animals, such as horses, sheep, calves, oxen, pigs, and rabbits. From fresh blood or stale blood, if still liquid or moist, and even from blood spots, if these have not been dry too long, hæmoglobin crystals may be obtained. The blood is, if necessary, allowed to dry on a slide, then rubbed with a little water and a few drops pressed through calico on to an object glass. After putting on the cover glass, the dried edges are examined first and should they contain crystals, the blood is sure to be of animal origin. In any case, hæmoglobin crystals will be deposited sooner or later, generally within 24 to 48 hours; those of human blood are characterised by belonging to the rhombic system and by large sharp edges and the presence of broad rectangular plates. Another conclusive fact is that the crystals of animal blood are invariably accompanied by crystals of oxyhæmoglobin.

L. DE K.
